

The Genco Declaration provides that UM was contacted by Aileen Gibson ("Gibson") and Mark T. Wajer ("Wajer") of Martin Marietta Magnesia Specialties ("MMMS"), prior to the Critical Date, regarding MMMS funding a study on the use of magnesium hydroxide in the bleaching of mechanical pulp. Wajer is the Business Development Manager, and Gibson is the Product Development Manager, for MMMS. Wajer and Gibson are the co-inventors in the Application. MMMS is the assignee of the Application. Prior to the Critical Date, UM agreed to conduct a multi-phase testing program ("Testing Program") for MMMS at the PDC directed to peroxide bleaching of mechanical pulp using magnesium hydroxide as a replacement for various pulp bleaching chemicals.

The Genco Declaration states that the first phase of the Test Program was performed at the PDC substantially continuously during a time period beginning and ending prior to the Critical Date, without having been halted or abandoned for other research projects, lack of funding or personnel, or other administrative or financial reasons. A report setting forth the results of the first phase of the Test Program ("Report 1") was issued to MMMS by UM on January 6, 2000. Report 1 is provided as an attachment ("Exhibit A") to the Genco Declaration.

A Declaration has also been presented herewith by Wajer and Gibson. The Wajer and Gibson Declaration confirms statements described above which are contained in the Genco Declaration. Additionally, the Wajer-Gibson Declaration provides that prior to the Critical Date, Gibson prepared a written document based on Report 1 ("Exhibit A") which was employed in drafting Provisional I. The Wajer-Gibson Declaration also sets forth that Provisional I was prepared on behalf of MMMS by the law firm of McDermott, Will & Emery, based on Report 1 ("Exhibit A"). Accordingly, Provisional I has an effective date of invention which is earlier in time than the Critical Date of CA '399.

The Genco Declaration also provides that the second phase of the Test Program was performed at the PDC substantially continuously during a time period beginning at the end of the

first phase of the Test Program and ending subsequent to the Critical Date, without having been halted or abandoned for other research projects, lack of funding or personnel, or other administrative or financial reasons. A report setting forth the results of the second phase of the Test Program ("Report 2") was issued to MMMS by UM on May 8, 2000. Report 2 is provided as an attachment ("Exhibit B") to the Genco Declaration. The Test Program conducted at the PDC has been funded entirely by MMMS.

The Wajer and Gibson Declaration confirms statements made above in the Genco Declaration with respect to the second phase of the Test Program. Additionally, the Wajer-Gibson Declaration provides that Gibson prepared a written document based on Report 2 ("Exhibit B") which was employed in drafting Provisional II. The Wajer-Gibson Declaration also states that Provisional II was prepared on behalf of MMMS by the law firm of McDermott, Will & Emery, based on Report 2 ("Exhibit B"). Accordingly, Provisional II has an effective date of invention which is earlier in time than the Critical Date of CA '399.

Therefore, CA '399 is not a prior art reference applicable to the pending claims of the subject patent application.

Regarding the prior art references other than CA '399 cited by the Examiner, Lundgren et al is directed to the bleaching of chemical pulp. Lundgren does not teach or suggest the bleaching of mechanical pulp. The requisite suggestion or teaching relied on in making this rejection comes from the Examiner not from the Lundgren reference. Technology that is useful in bleaching of chemical pulping is not necessarily useful in bleaching of mechanical pulp. The claims 1-48 relate to making a bleached mechanical pulp.

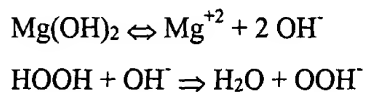
Lundgren et al bleaches chemical pulp with peroxide and elemental oxygen. The claims of the present invention are directed to bleaching mechanical pulp with peroxide and a magnesium compound. Elemental oxygen is not used as a bleaching chemical in the bleaching

of mechanical pulp. Elemental oxygen is not used or claimed by Applicants as a bleaching chemical for the bleaching of mechanical pulp. On the other hand, oxygen is commonly used in bleaching chemical pulps as taught by Lundgren et al. Chemical systems which are employed in the bleaching of chemical pulp do not work with certainty in the bleaching of mechanical pulp.

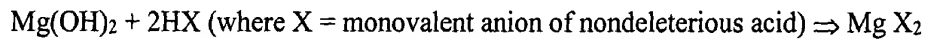
Fossum et al is also directed to bleaching of chemical pulp (see line 1, column 1, on page 1). Fossum et al does not teach or suggest the bleaching of mechanical pulp. The requisite suggestion or teaching has instead been introduced by the Examiner not by the Fossum et al reference. The claims 1-48 relate to making a bleached mechanical pulp.

Fossum et al specifies that chemical pulp to be bleached is immediately subjected to alkaline extraction to remove dissolved lignins. In mechanical pulps, extractions are not performed since they substantially reduce the ultimate yield of wood converted to paper. Contrarily, mechanical pulp yields are maintained as high as possible. Extraction is only performed as part of a bleaching sequence involving chemical pulps. It is not performed on mechanical pulps as claimed by applicants. Applicant teaches bleaching mechanical pulp to maintain yields as high as possible and to correspondingly reduce costs. Chemical bleaching systems which work in the bleaching of chemical pulp do not for certain work in the bleaching of mechanical pulp.

Fossum et al conducts its bleaching sequence at a pH of up to 3. Line 47, column 6 of Fossum et al, it describes magnesium salts as a complexing agent. In the claimed invention, magnesium hydroxide is employed as a replacement for caustic soda to activate the hydrogen peroxide according to following reaction scheme:



At pH of 3 or below,  $\text{Mg}(\text{OH})_2$  does not substantially exist. It is only present as a magnesium salt of the nondeleterious acid used. It has no alkalinity to activate the hydrogen peroxide as shown in the reactions above. Contrarily, in very acidic solutions, such as described in the Fossum et al reference, the following reaction occurs using a monovalent acid as an example:



A magnesium salt according to the teaching of Fossum, et al can only function as a complexing agent to preserve the viscosity in chemical pulps, not as an alkali source. Therefore, for  $\text{Mg}(\text{OH})_2$  to function as a peroxide activator, at a higher pH.

Gard does not teach or suggest that peroxide and magnesium oxide or magnesium hydroxide can be alternatively used on either mechanical or chemical pulp. Gard uses  $\text{MgO}$  as a standard only for purposes of measuring G-E brightness of pulp. Pure  $\text{MgO}$  is the "100" scale standard and carbon black is the "0" scale standard for brightness measurement using a General Electric reflectometer.  $\text{MgO}$  is not used in pulp bleaching in the process of Gard. Gard teaches conventional mechanical pulp bleaching using  $\text{NaOH}$ , not  $\text{MgO}$  or  $\text{MgOH}$ , to form an alkaline solution at a pH greater than 8.5, i.e., a pH of 10.5 to 11.

Absent some motivation, incentive, or suggestion in the prior art supporting the modification of a reference, obviousness cannot be established by combining the teachings of the prior art to modify the reference for purposes of producing the claimed invention. To make an obviousness rejection based on a combination of references, the Examiner must be able to point to a reference which suggests the combination. Absent such a suggestion, the Examiner has impermissibly used applicant's teachings to examine the prior art for the claimed elements, and combine them as claimed.

In summary, for the reasons set forth above, the applicable cited references, individually or in combination, do not teach or suggest the process set forth in claims 1-48 of the above-captioned invention.

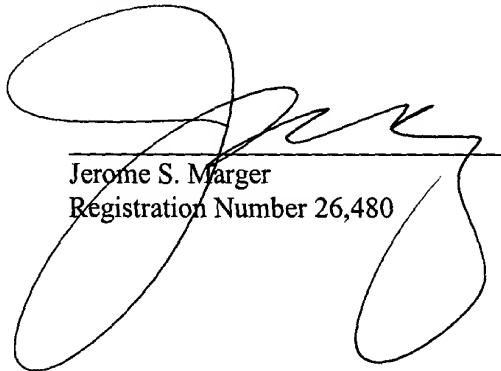
Accordingly, this application is now in condition for allowance, and the Examiner is requested to pass this application to issue forthwith. If any matters are later deemed unresolved by the Examiner, he is encouraged to call the Attorney for Applicants to discuss same.

**20575**

PATENT TRADEMARK OFFICE

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Respectfully submitted,



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**MAINE**

DEPARTMENT OF CHEMICAL ENGINEERING  
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**EXHIBIT A**

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January 6, 2000

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Burton Branch – Neil and Gunter  
From: Haixuan Zou, Donna Johnson, Joe Genco  
cc: Park, Ingraham

**RECEIVED**

**AUG 29 2002**

**TC 1700**

RE: Preliminary results of mechanical pulp bleaching with magnesium hydroxide

Hydrogen peroxide bleaching experiments were performed on hardwood TMP pulp from a northeastern mill, to attempt to get mill bleaching results using Irving mill conditions, and to then substitute magnesium hydroxide for various chemicals in the bleaching process. The work plan was based on the 'Proposal on the Use of  $\text{Mg}(\text{OH})_2$  in Peroxide bleaching of mechanical pulp' from JM Genco, Mill conditions were described in a memo from JM Genco,

### Procedures

TMP was obtained from the mill after refining. The brightness of this brownstock was 62.0 % ISO.

The magnesium hydroxide used was supplied by Martin Marietta, and was a slurry with a 0.415 micron particle size. This particle size was used after a discussion at the Tappi Pulping Conference in November, where the decision was made to start with the smallest particle size supplied.

The conditions used in bleaching followed the Irving, St. John, mill conditions as closely as practicable for the control, or base, case. Substitution of  $\text{Mg}(\text{OH})_2$  was done generally following the suggestions in Vincent, et al (1997).

The chelation step was done as follows:

1. Weigh out the calculated volume of distilled water needed for 10% consistency to 70°C.
2. Add DTPA to water and mix.
3. Weigh out 50g pulp into bleaching bag, add DTPA solution, and mix. Seal bag.
4. Place in 70°C water bath for 30 minutes.
5. Squeeze the pulp through a 200-mesh bag to about 25% consistency.

The hydrogen peroxide stage was done as follows for the base case (mill conditions):

1. Weigh out desired pulp and water for 10% consistency, and preheat each separately to 70°C.
2. Weigh out silicate and sodium hydroxide, and add them to the water and mix.
3. Add peroxide to the solution, mix, and quickly add to the pulp, and mix thoroughly.
4. Check pH, and adjust in necessary with NaOH.
5. Put pulp in sealed bleaching bag into the 70°C water bath, and mix every 15 minutes by kneading.
6. Bleach for 2 hours, then remove from bath.
7. Squeeze pulp to get liquor for residual test.
8. Neutralize pulp with sulfuric acid and wash with distilled water
9. Test pulp for brightness, and color, and liquor for residual pH and hydrogen peroxide.

In further bleaching cases, DTPA was also added at the hydrogen peroxide stage. In these instances, steps 2-3 would become:

2. Weigh out DTPA, mix with water. Weigh out  $Mg(OH)_2$ , mix into the solution. Add pulp and mix.
3. Add peroxide to pulp and mix thoroughly.

## Results

The experiments performed are shown in matrix form in Figure 1. All results are reported in Table 1, which also shows the conditions used. Figure 2 holds the brightness data, Figure 3 the peroxide residual data, and Figure 4 the pH data.

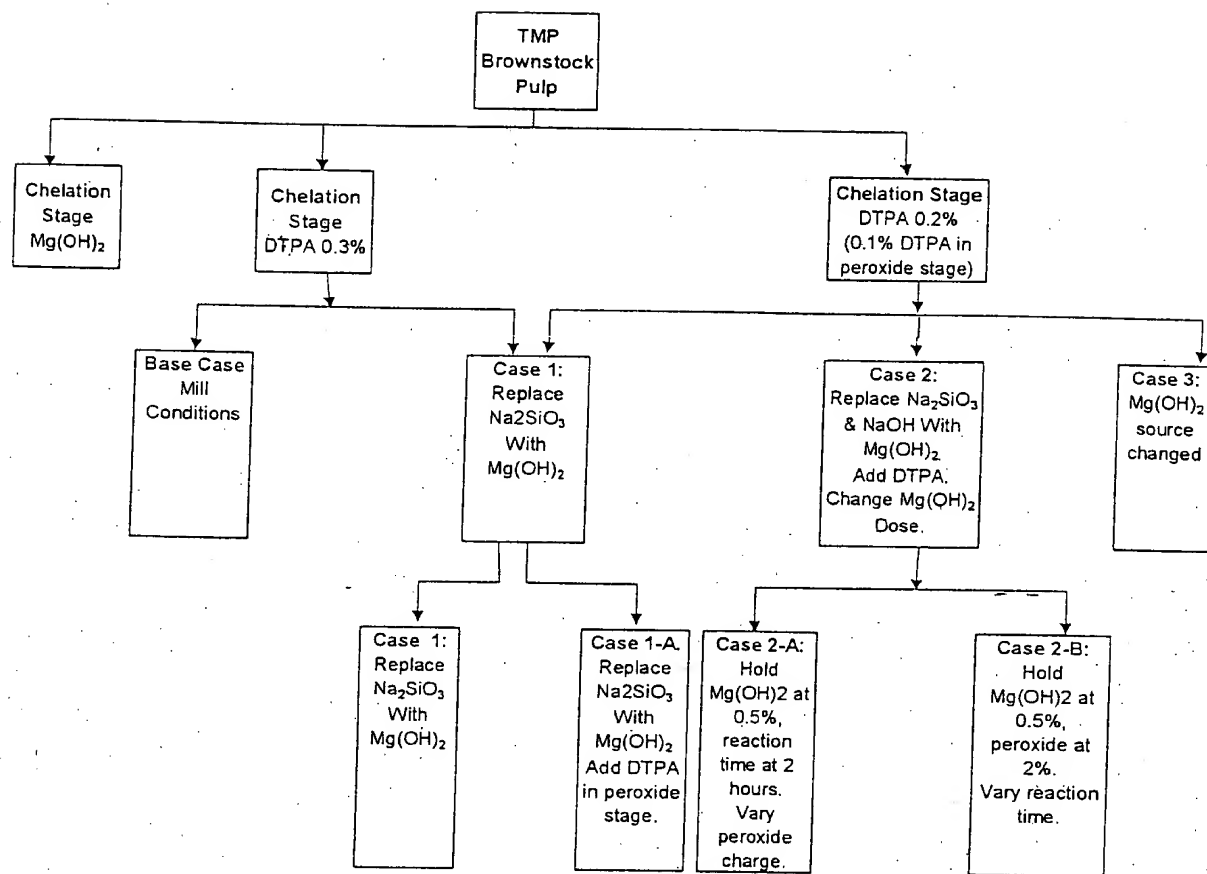


Figure 1. Experiments done with TMP pulp.



Table 1. Bleaching results for TMP pulp.

	Sample ID	DTPA	Na <sub>2</sub> SiO <sub>3</sub>	NaOH	H <sub>2</sub> O <sub>2</sub>	Mg(OH) <sub>2</sub>	Initial pH	Final pH	Residual H <sub>2</sub> O <sub>2</sub> (g/l)	Brightness % ISO	Color		
											L	a	b
TMP	U-1-1									62.04	87.85	0.31	12.83
Chelation	Blank							4.80		63.42	88.38	0.28	12.34
	DTPA	0.3%								63.79	88.66	0.25	12.39
	Mg(OH) <sub>2</sub>	Mg(OH) <sub>2</sub> = 0.363%						8.15		58.02	85.07	0.26	12.55
Base Case	1 hr	0.3%	3%	1.56%	2.0%	0.00%	11.23	8.70	0.476	72.66	92.69	-1.81	10.89
	2 hrs	0.3%	3%	1.56%	2.0%	0.00%	11.06	8.00	0.394	72.46	92.78	-2.15	11.13
	3 hrs	0.3%	3%	1.56%	2.0%	0.00%	11.09	7.70	0.374	73.09	92.95	-1.76	10.89
Case 1**	2hrs	0.3%	0	1.56%	2.0%	0.50%	11.60	8.00	0.007	62.53	87.86	-0.17	12.44
	2hrs	0.3%	0	1.56%	2.0%	1.00%	11.80	8.20	0.003	60.76	87.00	0.18	12.70
	2hrs	0.3%	0	0.84%	2.0%	1.50%	11.20	8.30	0.003	60.31	86.55	0.04	12.50
Case 1-A**	2hrs	0.2%, 0.1%	0	0.72%	1.0%	0.50%	10.50	8.25	0.014	63.75	88.38	-0.34	12.15
	2hrs	0.2%, 0.1%	0	0.80%	1.5%	0.50%	10.50	8.30	0.020	64.72	89.03	-0.59	12.21
	2hrs	0.2%, 0.1%	0	1.00%	2.0%	0.50%	10.53	8.00	0.075	66.37	89.89	-0.81	12.03
Case 2**	2hrs	0.2%, 0.1%	0	0	2.0%	0.00%	4.90	5.17	1.972	65.90	90.08	-0.06	12.47
	2hrs	0.2%, 0.1%	0	0	2.0%	0.25%		6.43	1.666	69.53	91.71	-0.98	11.98
	2hrs	0.2%, 0.1%	0	0	2.0%	0.50%	6.50	7.28	0.966	70.26	91.92	-1.35	11.66
Case 2-A*	2hrs	0.2%, 0.1%	0	0	2.0%	1.00%	7.07	7.67	0.245	67.08	90.40	-0.84	12.10
	2hrs	0.2%, 0.1%	0	0	2.0%	1.50%	7.07	8.15	0.014	62.58	87.96	-0.38	12.45
	2hrs	0.2%, 0.1%	0	0	1.5%	0.50%	6.83	7.59	0.578	68.44	91.21	-0.90	12.14
Case 2-B**	2hrs	0.2%, 0.1%	0	0	2.5%	0.50%	7.06	7.52	1.299	71.24	92.49	-1.23	11.66
	2hrs	0.2%, 0.1%	0	0	3.0%	0.50%	7.23	6.70	1.877	72.36	92.97	-1.50	11.41
	3hrs	0.2%, 0.1%	0	0	2.0%	0.50%	6.51	6.94	0.870	70.62	92.39	-1.38	11.98
Case 3*	4hrs	0.2%, 0.1%	0	0	2.0%	0.50%	6.49	6.42	0.870	71.15	92.73	-1.42	11.99
	6hrs	0.2%, 0.1%	0	0	2.0%	0.50%	6.53	6.08	0.775	71.63	93.02	-1.58	12.05
	3.101 microns	0.2%, 0.1%	0	0	2.0%	0.50%	5.71	7.09	0.891	69.77	91.71	-1.050	11.70
Case 3*	0.65 microns	0.2%, 0.1%	0	0	2.0%	0.50%	6.28	7.05	1.122	70.29	92.03	-1.150	11.74
	0.603 microns	0.2%, 0.1%	0	0	2.0%	0.50%	6.31	6.99	1.021	70.31	92.04	-1.110	11.70
	BayMag	0.2%, 0.1%	0	0	2.0%	0.50%	4.92	7.10	0.394	67.16	90.32	-0.700	11.89
Case 3*	Martin Marietta MgO	0.2%, 0.1%	0	0	2.0%	0.50%	7.78	6.69	0.510	71.13	92.53	-1.320	11.73

\*reaction time 2 hrs.

\*\*Mg(OH)<sub>2</sub>-----P277-262-1(0.415 micron) was applied.

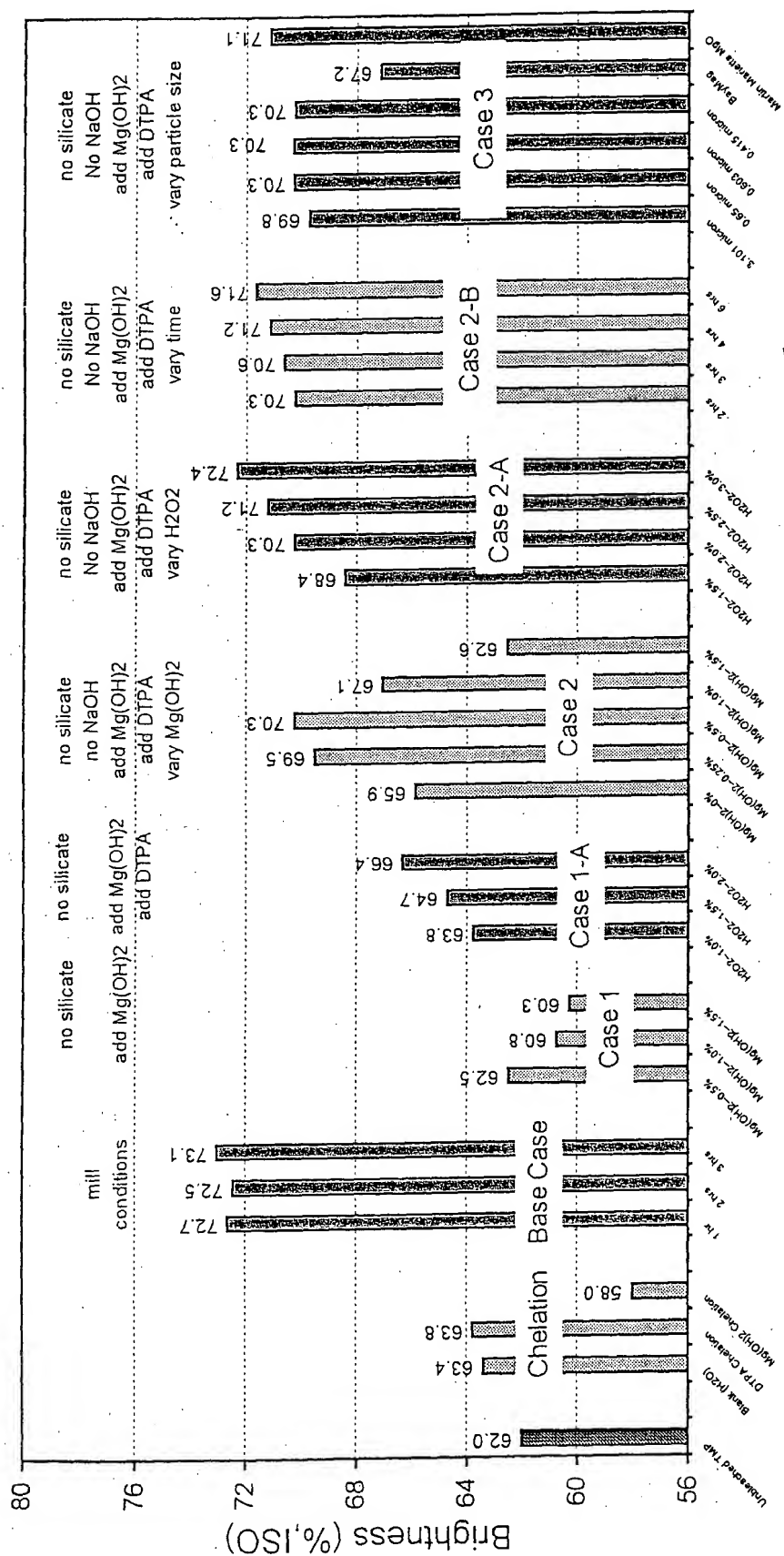


Figure 2. Brightness results for TMP pulp.



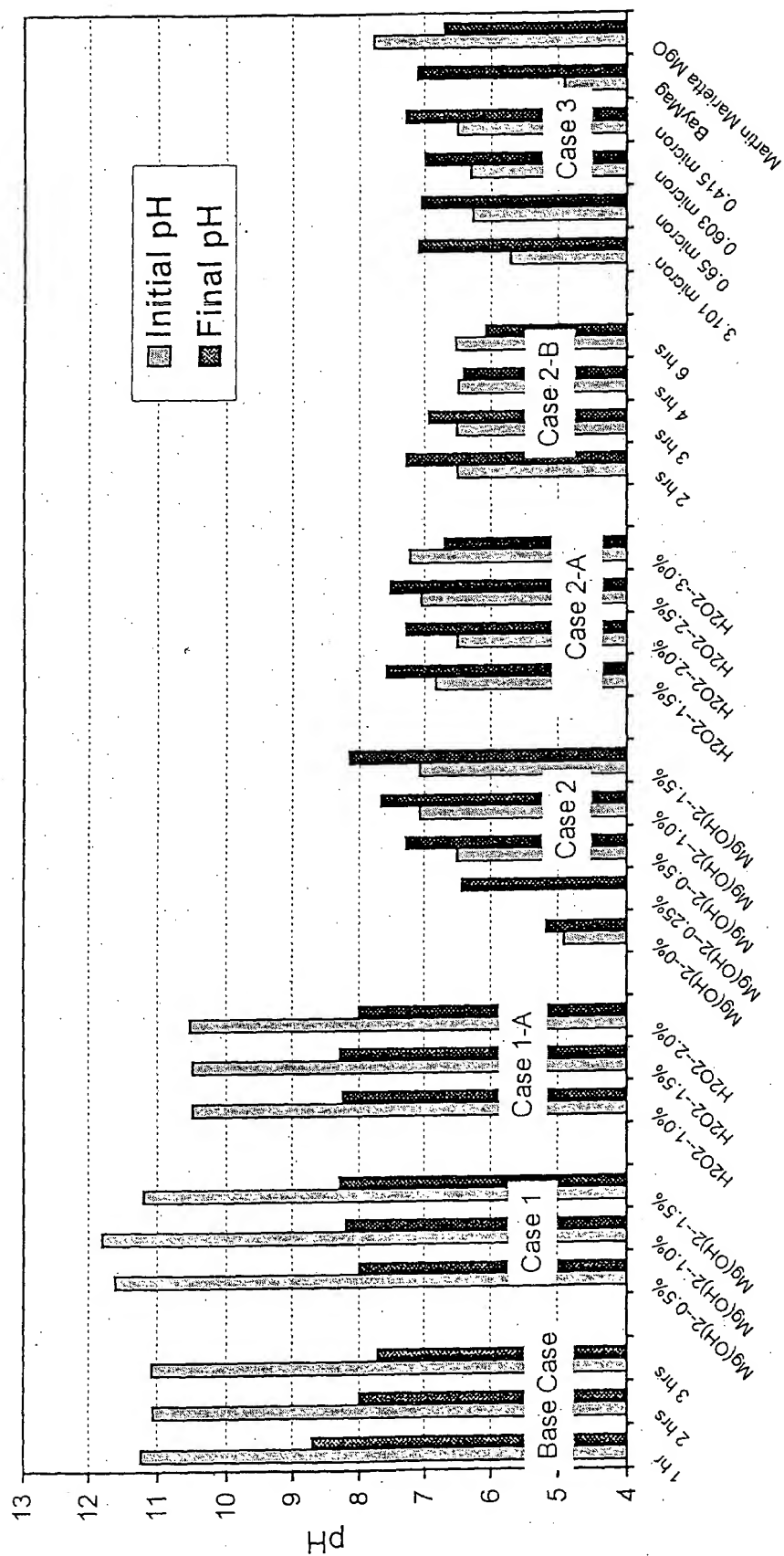


Figure 4. Initial and final pH values of TMP pulp.

**Chelation.** The chelation stage was first tested. Three experiments were done, following the procedure outlined previously, using the appropriate chemical: (1) blank, using distilled water, (2) mill conditions, using 0.3% DTPA, and (3)  $\text{Mg}(\text{OH})_2$  substitution, using 0.363%  $\text{Mg}(\text{OH})_2$ . The brightness results are shown in Figure 2. The blank and DTPA chelation show approximately the same brightness gain, going from a brownstock value of 62.0 to 63.4 for the blank and 63.8 for the DTPA chelation. The  $\text{Mg}(\text{OH})_2$  chelation darkened the pulp to 58.0. Since the  $\text{Mg}(\text{OH})_2$  darkened the pulp, no further work was done on  $\text{Mg}(\text{OH})_2$  chelated pulp. All further experiments were done using DTPA chelated pulp, at either 0.2% or 0.3% in the chelation stage.

**Base Case.** Mill conditions were followed for the base case, and three reaction times were examined, 1, 2, and 3 hours. A 0.3% DTPA chelation stage was used, and 3%  $\text{Na}_2\text{SiO}_3$ , 1.6%  $\text{NaOH}$ , and 2%  $\text{H}_2\text{O}_2$  in the peroxide stage. Results are found in Table 1. Figure 2 shows the brightness values for the three reaction times. There was little difference in brightness values for the three reaction times, ranging from 72.5 to 73.1% ISO. Peroxide residual, shown in Figure 3, was also similar for the three reaction times - however, it did decrease slightly with reaction time, from 0.48g/l at one hour to 0.37g/l at three hours. As Figure 4 shows, the initial pH was similar for all three experiments, and the final pH was lower for the longer reaction times, 8.7 at one hour to 7.7 at three hours. These results lead to choosing a two hour reaction time for the next set of experiments.

**Case 1.** Case 1 experiments replace sodium silicate with magnesium hydroxide. The 0.3% DTPA chelation stage was kept the same. The hydrogen peroxide dose was held at 2%, while the  $\text{Mg}(\text{OH})_2$  dose was changed from 0.5 to 1.5%. The  $\text{NaOH}$  charge was varied to reach the initial pH target of 11.2 to 11.8. Results are found in Table 1. Figure 2 shows brightness values.

There is a definite disadvantage to brightness for this case. The base case two hour reaction time resulted in a brightness of 72.5% ISO, whereas the best condition for Case 1 experiments, 0.5%  $\text{Mg}(\text{OH})_2$ , resulted in a brightness of 62.5% ISO. Higher levels of  $\text{Mg}(\text{OH})_2$  resulted in lower brightness values. There is little peroxide residual under these conditions. The initial and final pH values are similar to the base case.

Case 1-A. Since  $\text{Mg}(\text{OH})_2$  was being added in the peroxide stage, two experiments were done adding DTPA to the peroxide stage, in addition to the chelating stage. The same total amount of chelant was added, 0.3%, but 0.2% was used in the chelation stage, and 0.1% added during the peroxide stage. 0.5%  $\text{Mg}(\text{OH})_2$  was used in both experiments, but two lower doses of peroxide were used, 1% and 1.5%. These results are shown in Figure 2. As is shown, the addition of chelant in the peroxide stage increased the brightness over the Case 1 results, even with a lower peroxide charge. At the 1.5% peroxide charge, the brightness attained 64.7% ISO, a 2 point increase over the Case 1 results. However, that value is still almost 8 points lower than the base case.

These results caused the remaining experiments to be done with the chelant charge split between the chelation stage and the peroxide stage.

Case 2. Case 2 experiments replace both sodium silicate and sodium hydroxide with magnesium hydroxide. The chelation stage used 0.2% DTPA. The peroxide stage was charged with 0.1% peroxide, 2%  $\text{H}_2\text{O}_2$ , and four doses of  $\text{Mg}(\text{OH})_2$ , from 0 to 1.5%, were tested. Reaction time was two hours. The results are in Figure 2 through Figure 4.

The best results for this set of experiments is again at 0.5%  $\text{Mg}(\text{OH})_2$ , where the brightness is 70.3% ISO, approaching the base case of 72.5% ISO. It is an eight point increase over the Case 2 results at the same  $\text{Mg}(\text{OH})_2$  and peroxide dosages, but without  $\text{NaOH}$ , and with chelant added at the peroxide stage. These conditions also result in a substantial peroxide residual, 0.97g/l at 0.5%  $\text{Mg}(\text{OH})_2$ , as seen in Figure 3. The pH for these experiments is lower than for the other experiments, as is shown in Figure 4. Without the silicate or caustic, the initial pH with the  $\text{Mg}(\text{OH})_2$  is 6.5 to 7, and the final pH increases to 7.3 to 8.2, higher with the higher  $\text{Mg}(\text{OH})_2$  charge.

The results of these experiments showed that the brightness of the base case could be approached. There was still residual peroxide at 0.5%  $\text{Mg}(\text{OH})_2$  charge, and so potential for further reaction. Case 2-A increased the reaction time. Case 2-B increased the peroxide charge applied.

Case 2-A. These experiments follow the conditions of Case 2 experiments, but with the  $\text{Mg}(\text{OH})_2$  charge held at 0.5%, and the peroxide charge varied.

Increasing the peroxide charge increased the brightness gain. At 3% peroxide charge in Case 2-A, the brightness increased to 72.4, which is very similar to the Base Case value of 72.5% ISO, at the two hour reaction time.

**Case 2-B.** These experiments follow the conditions of Case 2 experiments, but with the  $\text{Mg}(\text{OH})_2$  charge held at 0.5%, and the reaction times varied.

Increasing the reaction time increased the brightness, and a six hour reaction time gave a brightness of 71.6% ISO. This is about a point below the Base Case value of 72.5% ISO at two hour reaction time.

The peroxide residual (Figure 3) decreases slightly with increasing reaction time.

**Case 3.** Case 3 experiments screen some other particle sizes of Martin Marietta  $\text{Mg}(\text{OH})_2$ , as well as BayMag and Martin Marietta  $\text{MgO}$ . The 0.415 micron  $\text{Mg}(\text{OH})_2$  was the material used in all other experiments.

There was little difference in the brightness response for the different sizes of  $\text{Mg}(\text{OH})_2$ , all about 70% ISO. The BayMag response was worse than all others, by about 3 points, and the Martin Marietta  $\text{MgO}$  response was somewhat better, 71.1% ISO.

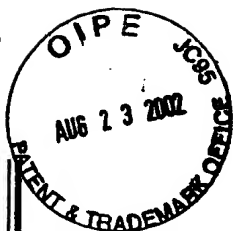
## Observations

Base Case brightness results could be approached without silicate or caustic addition, by peroxide bleaching with the addition of DTPA and  $\text{Mg}(\text{OH})_2$  in the peroxide stage. Base Case results could be reached by increasing peroxide charge, and closely approached by increasing reaction time to six hours.

A 0.5%  $\text{Mg}(\text{OH})_2$  charge seems optimum with conditions used at this point. This agrees with the Vincent et al (1997) study.

Particle size of  $\text{Mg}(\text{OH})_2$  did not seem to have much effect. The Martin Marietta  $\text{MgO}$  gave slightly higher brightness results than  $\text{Mg}(\text{OH})_2$ .

Work is in progress to test 'best case' conditions from this study on pulp from the Irving, St. John, mill.



## EXHIBIT B

### HYDROGEN PEROXIDE BLEACHING OF TMP PULPS USING $\text{MG}(\text{OH})_2$ : OPTIMIZATION EXPERIMENTS

by

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TC 1700

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Presented to Martin Marietta on May 8, 2000 (per A. Gibson)

May, 2000



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# **HYDROGEN PEROXIDE BLEACHING OF TMP PULPS USING $\text{Mg}(\text{OH})_2$ : OPTIMIZATION EXPERIMENTS**

## **INTRODUCTION**

In Phase 1 of this work, experiments were done to screen various methods of using  $\text{Mg}(\text{OH})_2$  in peroxide bleaching of TMP pulp. Pulps from two mills, Champion, Bucksport, ME, and Irving Paper Co., St. John, NB, were used. This work showed that mill condition brightness values could be approached by peroxide bleaching using  $\text{Mg}(\text{OH})_2$ , without the use of caustic or silicate in the bleaching liquor. In many experiments, the residual peroxide content was substantial, and brightness could perhaps be increased if the residual could be utilized. Phase 2 of this work was undertaken to optimize the  $\text{Mg}(\text{OH})_2$  peroxide bleaching on Irving pulps.

The experimental plan was developed from the proposal 'Optimization of Peroxide Bleaching of Irving TMP using  $\text{Mg}(\text{OH})_2$  and  $\text{MgO}$ ', and from a meeting and conference call with Neill and Gunter and Martin Marietta on

## **PROCEDURES AND EXPERIMENTS**

All work was done on an unchelated Irving pulp sample collected in January, using the 3.1 micron  $\text{Mg}(\text{OH})_2$  sample supplied by Martin Marietta in February. Bleaching procedures were outlined in the previous report. Bleaching conditions are found in the data tables in Appendix A.

Bleaching experiments were done using a chelation stage followed by a hydrogen peroxide stage, both at 10% consistency, and the pulp was then washed and tested. Procedures were modified slightly from the first phase of the work. The chelation stage was done on one day, and the peroxide stage on the following day, to accommodate personnel scheduling (as opposed to both stages being done on the same day). The pulp washing procedure was modified to always use the same amount of water.

## **CONTROL**

Mill conditions (10% consistency, 70°C, chelation, 0.2% hydrosulfite, 0.3% DTPA, 30 min.; peroxide stage, 0.3% silicate, 1.5% NaOH, 2% peroxide, 5 hours)

### SPLIT $\text{Mg}(\text{OH})_2$ ADDITION

Does additional  $\text{Mg}(\text{OH})_2$  after the initial dose at the beginning of the peroxide stage help to decompose some of the remaining peroxide residual, so the bleaching reaction can continue to target brightness without additional peroxide?

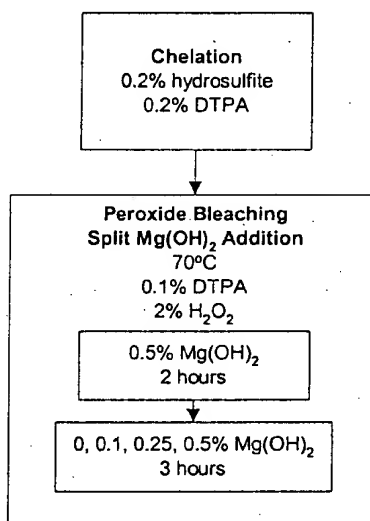


Figure 1. Flow diagram of  $\text{Mg}(\text{OH})_2$  split addition experiments.

### RECYCLING RESIDUAL PEROXIDE

Can the peroxide residual in the filtrate be reused to

Increase the brightness gain of 2% fresh peroxide, to reach target brightness? [A]

Replace some of the 2% fresh peroxide used, while still reaching target brightness? [B]

Can the recycled filtrate continue to be effective through multiple bleaching cycles? [C]

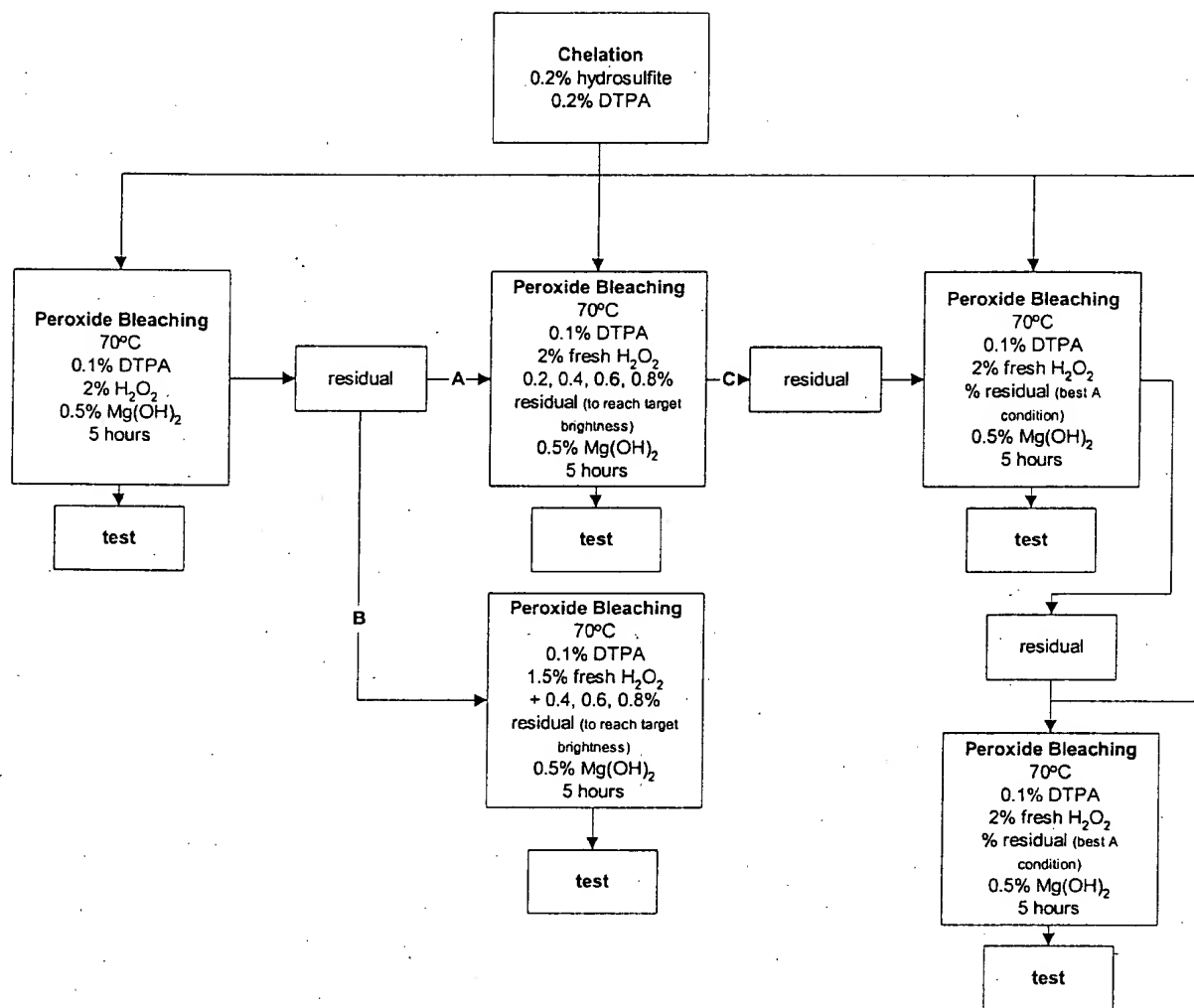


Figure 2. Flow diagram of filtrate recycling experiments.

### OPTIMIZE CHELANT DOSAGE

Can the  $\text{Mg}(\text{OH})_2$  dose be increased to assist with peroxide decomposition, if the chelant is increased to tie up the metals in the  $\text{Mg}(\text{OH})_2$ ? (keep ratio of DTPA to  $\text{Mg}(\text{OH})_2$  constant in P stage)

2% peroxide, 5 hours

Total chelant %	Q stage	P stage		
	% DTPA	% DTPA	% $\text{Mg}(\text{OH})_2$	Ratio DTPA: $\text{Mg}(\text{OH})_2$
0.25	0.2	0.05	0.25	0.2
0.3	0.2	0.1	0.5	0.2
0.35	0.2	0.15	0.75	0.2
0.4	0.2	0.2	1.0	0.2
0.5	0.2	0.3	1.5	0.2

How much chelant is needed, and in what stage? (hold  $\text{Mg}(\text{OH})_2$  constant in P stage, and change ratio of DTPA to  $\text{Mg}(\text{OH})_2$ ).

Total chelant %	Q stage	P stage		
	% DTPA	% DTPA	% $\text{Mg}(\text{OH})_2$	Ratio DTPA: $\text{Mg}(\text{OH})_2$
0.2	0.2	0	0.5	0
0.25	0.2	0.05	0.5	0.1
0.3	0.2	0.1	0.5	0.2
0.4	0.2	0.2	0.5	0.4
0.5	0.2	0.3	0.5	0.6
0.1	0.1	0	0.5	0
0.15	0.1	0.05	0.5	0.1
0.2	0.1	0.1	0.5	0.2
0.3	0.1	0.2	0.5	0.4
0.4	0.1	0.3	0.5	0.6

Other questions:

What is the best ratio of DTPA to  $\text{Mg}(\text{OH})_2$ ?

Would more pure  $\text{Mg}(\text{OH})_2$  improve results?

If chelant is added to  $\text{Mg}(\text{OH})_2$ , will it effectively tie up metals due to  $\text{Mg}(\text{OH})_2$ ?

Can the amount of chelant needed be determined by knowing metals content of pulp and  $\text{Mg}(\text{OH})_2$ ?

#### REPLICATE BLEACHING EXPERIMENTS

Control over time

Generate residual

#### TIMING OF BLEACHING SEQUENCES

In the data table, there are rows titled 'Q and P stages done same day' and 'Q and P stages done consecutive days'. These indicate a change in procedure, to accommodate scheduling issues. In the first phase, the chelation (Q) and peroxide (P) stages were done on the same day, and in this phase of the work, the Q stage is done one day, and the P stage the next. The comparative experiments show little difference between the timing of the Q and P stages.

#### HYDROSULFITE IN CHELATION STAGE

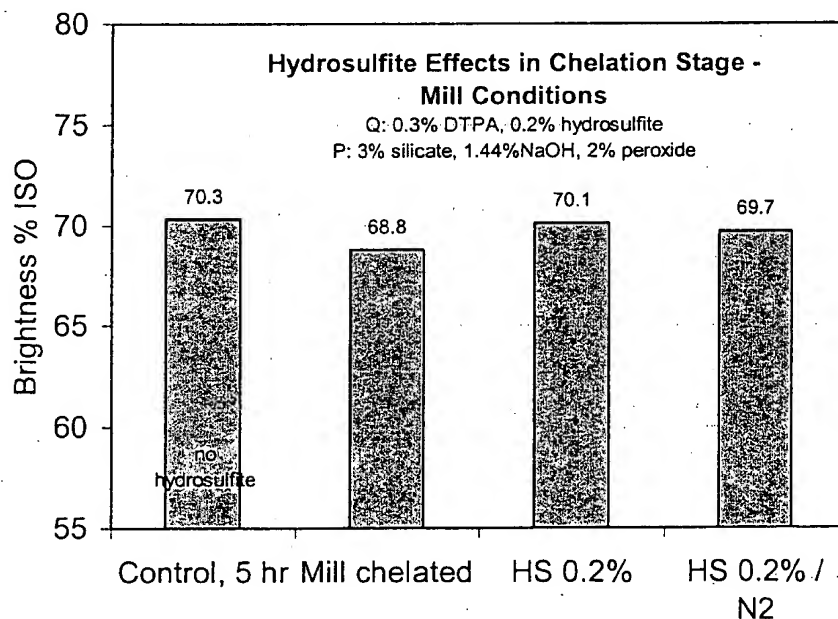


Figure 3. Hydrosulfite chelation stage (HS) vs. no hydrosulfite in chelation stage (control), mill conditions – brightness.

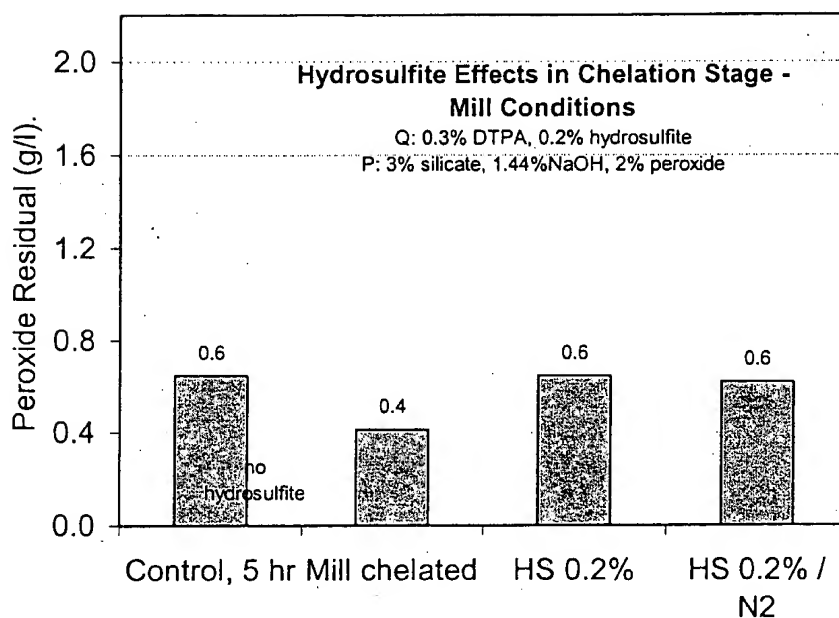


Figure 4. Hydrosulfite chelation stage (HS) vs. no hydrosulfite in chelation stage (control), mill conditions – Peroxide residual.

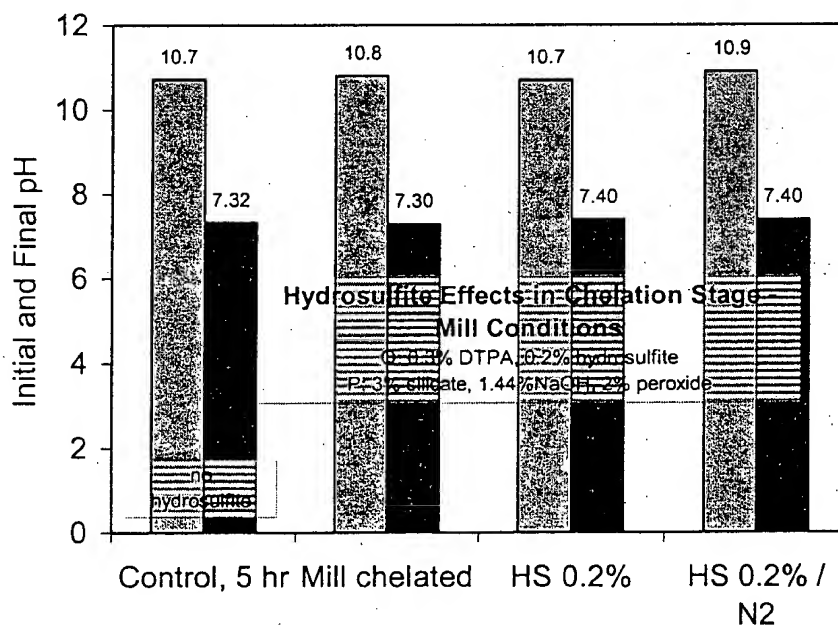


Figure 5. Hydrosulfite chelation stage (HS) vs. no hydrosulfite in chelation stage (control), mill conditions – Initial and final pH.

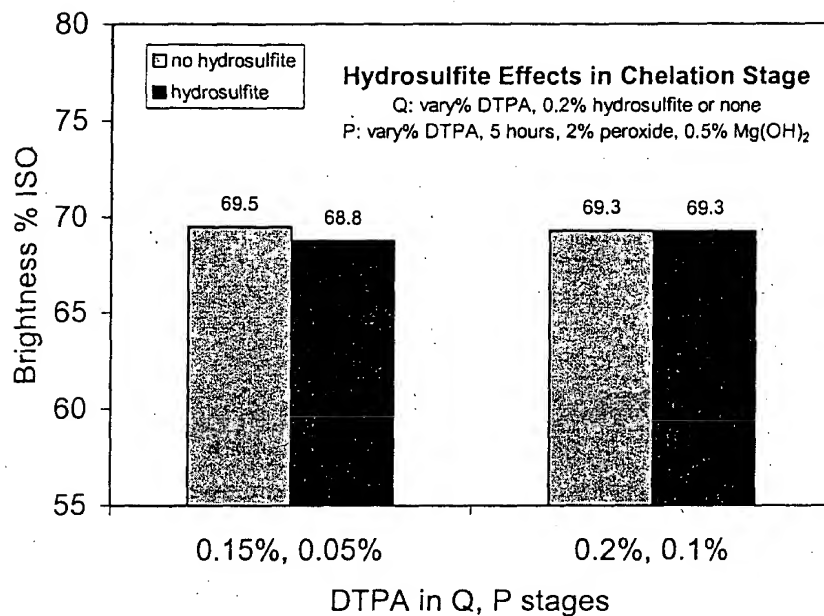


Figure 6. Hydrosulfite chelation stage vs. no hydrosulfite in chelation stage,  $\text{Mg}(\text{OH})_2$  experiments – brightness.

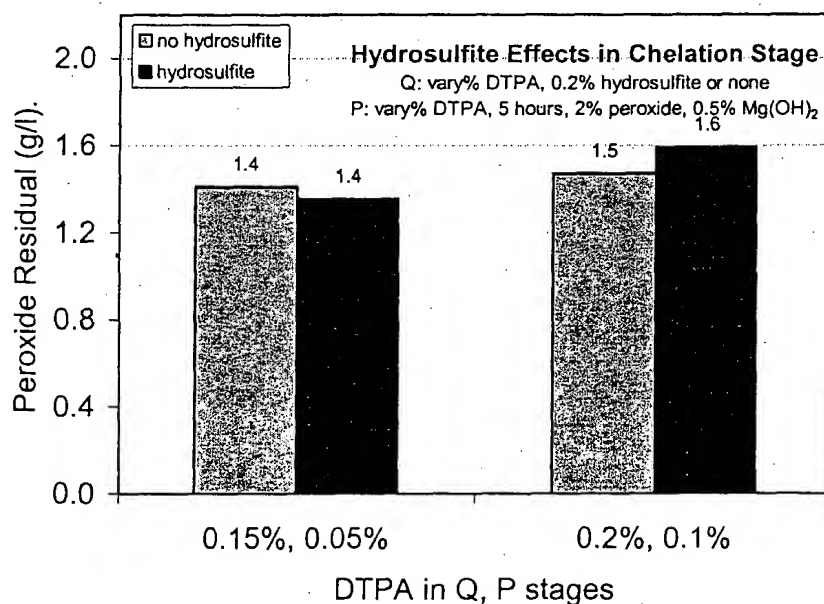


Figure 7. Hydrosulfite chelation stage vs. no hydrosulfite in chelation stage,  $\text{Mg}(\text{OH})_2$  experiments – Peroxide residual.



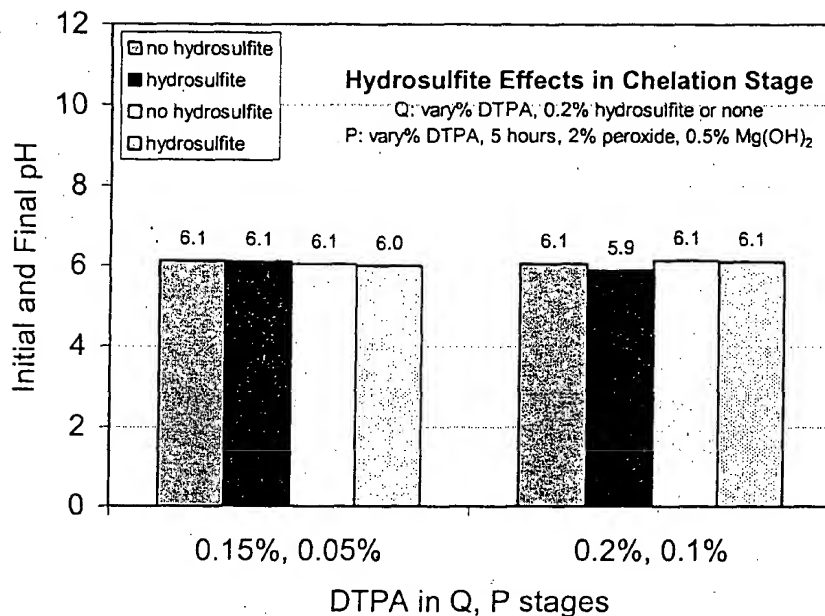


Figure 8. Hydrosulfite chelation stage vs. no hydrosulfite in chelation stage, Mg(OH)<sub>2</sub> experiments – Initial and final pH.

## RESULTS AND DISCUSSION

### SPLIT Mg(OH)<sub>2</sub> ADDITION EXPERIMENTS

The data from the split addition Mg(OH)<sub>2</sub> experiments (starting the bleaching with 0.1% DTPA, 2% peroxide, 0.5% Mg(OH)<sub>2</sub>, then after 2 hours adding additional Mg(OH)<sub>2</sub>) are found in Figure 9, Figure 10, and Figure 11.

The mill control conditions were reached with a 0.5% Mg(OH)<sub>2</sub> in the beginning, and an additional 0.25% Mg(OH)<sub>2</sub> during the reaction time. Brightness increased with increasing dosage of Mg(OH)<sub>2</sub> added during the reaction, and residual peroxide decreased. There was still residual available with a 0.5% Mg(OH)<sub>2</sub> additional dose.

It might be interesting to try reducing the peroxide charge to 1.5%, and see what Mg(OH)<sub>2</sub> addition levels would reach the control brightness level.

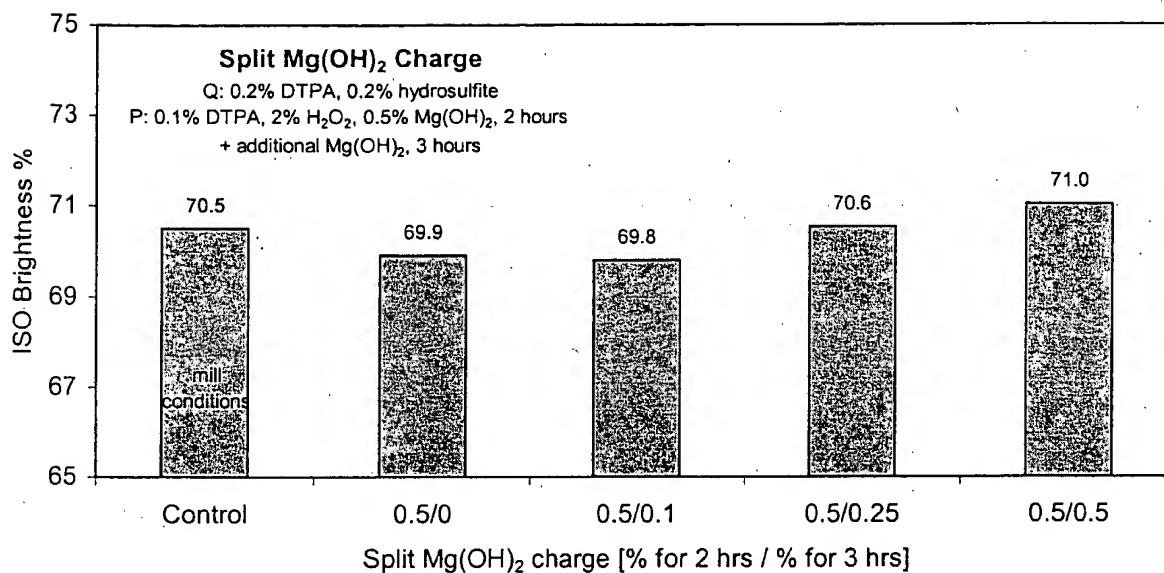


Figure 9. Split  $\text{Mg}(\text{OH})_2$  charge – brightness results.

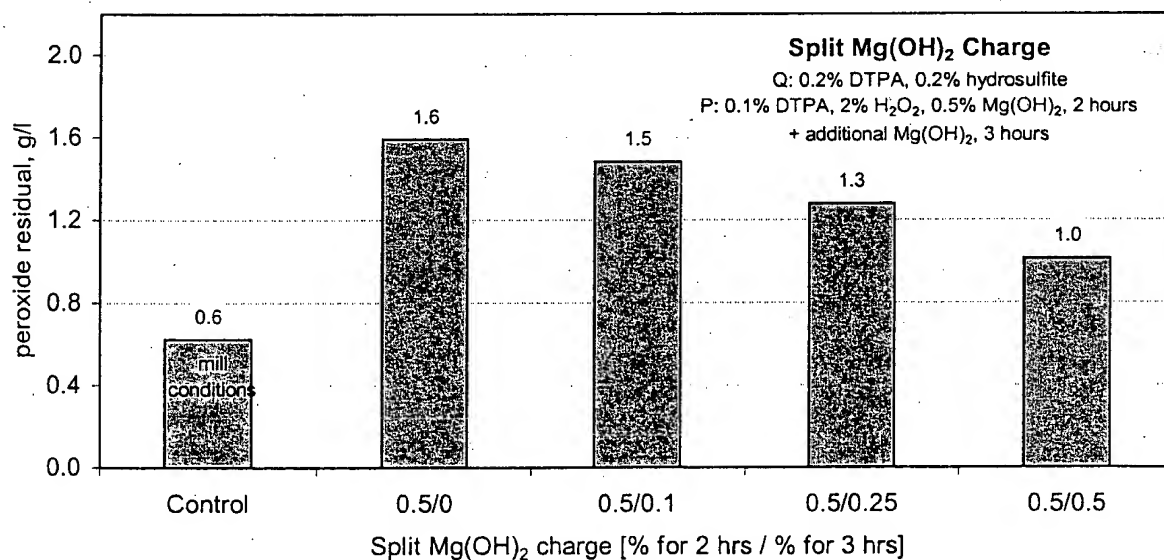
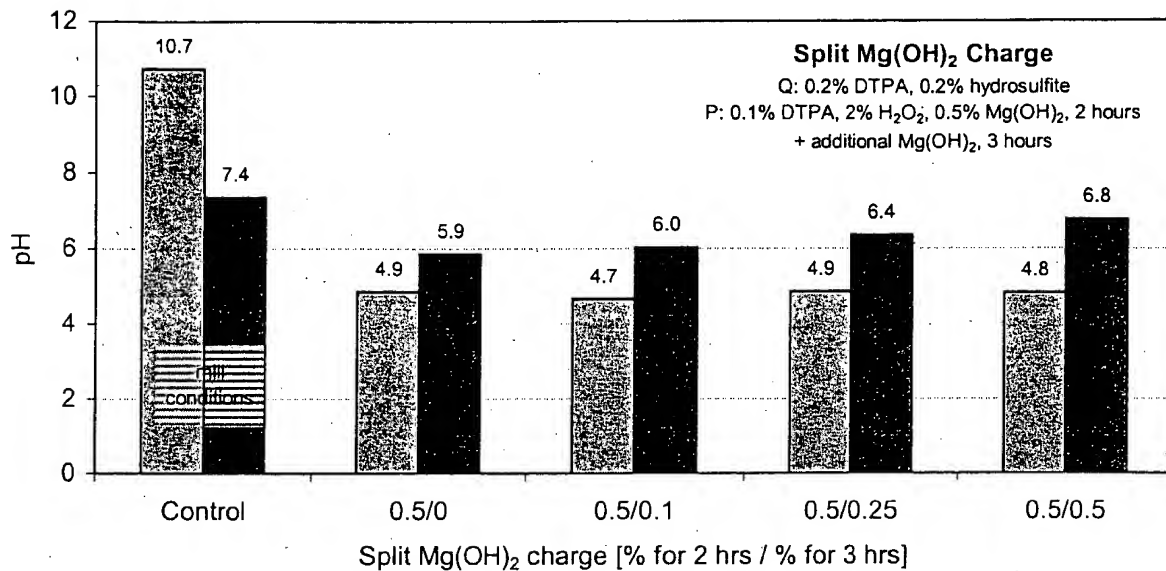


Figure 10. Split  $\text{Mg}(\text{OH})_2$  charge – residual peroxide.



**Figure 11. Split  $\text{Mg}(\text{OH})_2$  charge – initial and final pH.**

#### **FRESH PEROXIDE + FILTRATE PEROXIDE EXPERIMENTS**

Figure 12 - Figure 14 show preliminary results, using the Irving pulp sample from Phase 1 work, of substituting residual peroxide for fresh. They show that the substitution worked, as long as the proper amount of  $\text{Mg}(\text{OH})_2$  was added.

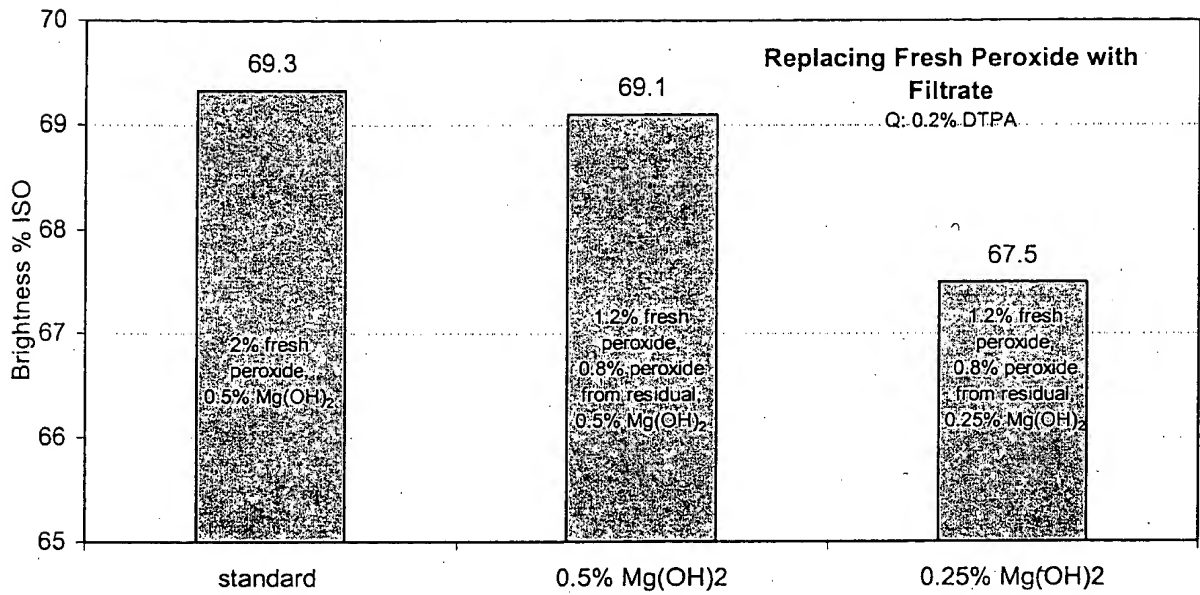


Figure 12. Replacing fresh peroxide with filtrate – brightness.

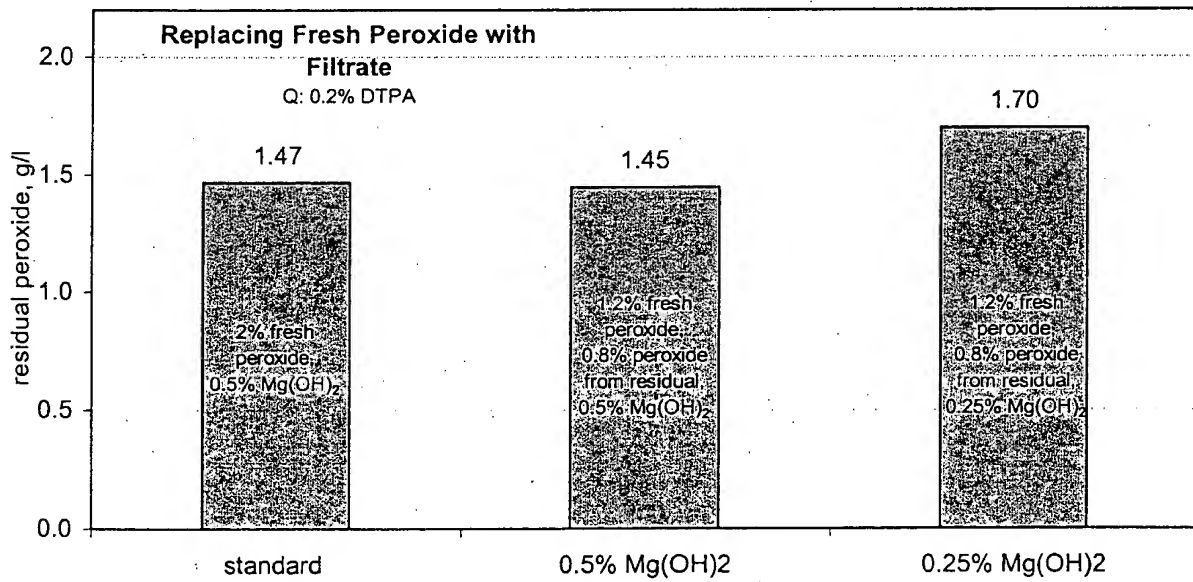
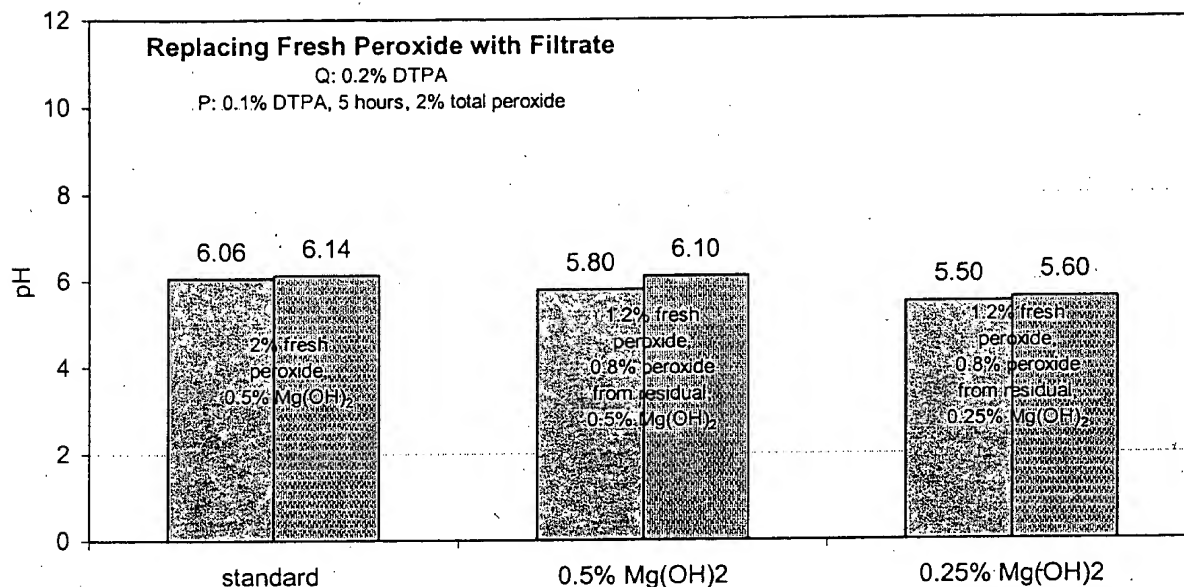


Figure 13. Replacing fresh peroxide with filtrate – residual peroxide.



**Figure 14. Replacing fresh peroxide with filtrate – initial and final pH.**

For this set of experiments, fresh peroxide plus additional peroxide from filtrate (residual) from previous bleaching experiments was used in the bleaching liquor. Several experiments were done with fresh peroxide only (labeled 'obtain residual' in TABLE), and the filtrate from these experiments was used in filtrate recycling experiments.

For the 2% fresh peroxide plus residual peroxide (Figure 15 -Figure 17), the brightness increases with increasing amount of peroxide from filtrate added, about a point when 0.8% peroxide from filtrate is added. The residual also increases, but the percentage of peroxide consumed stays constant. Perhaps more  $Mg(OH)_2$  should have been added with the increase in peroxide charge.

The total 2.8% peroxide charge reached a brightness of 70.1%, while the mill conditions reached a brightness of 70.5.

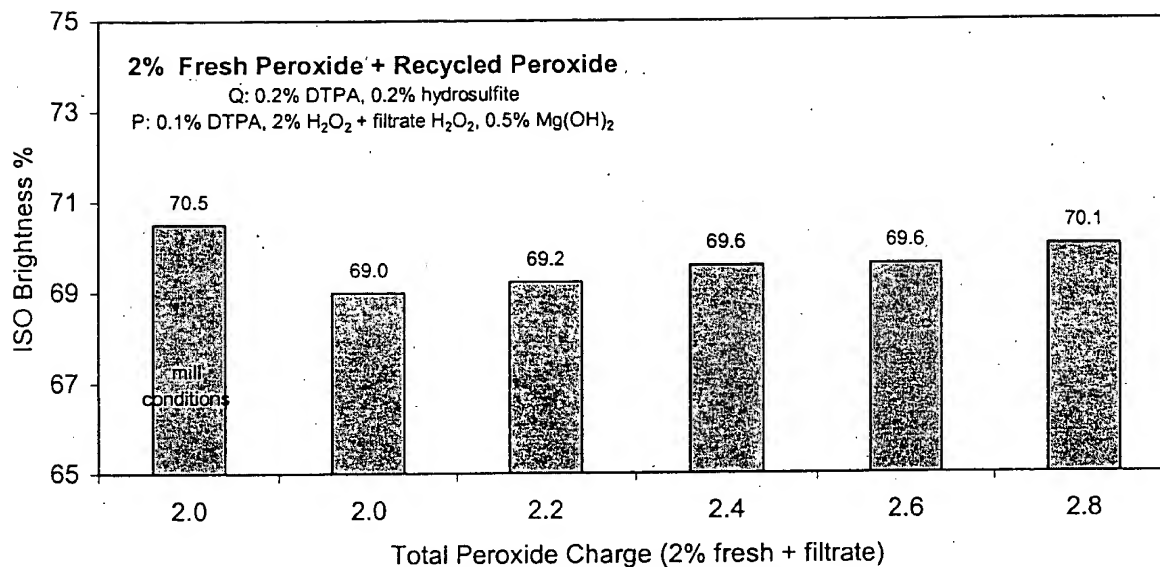


Figure 15. 2% fresh peroxide + residual peroxide – brightness.

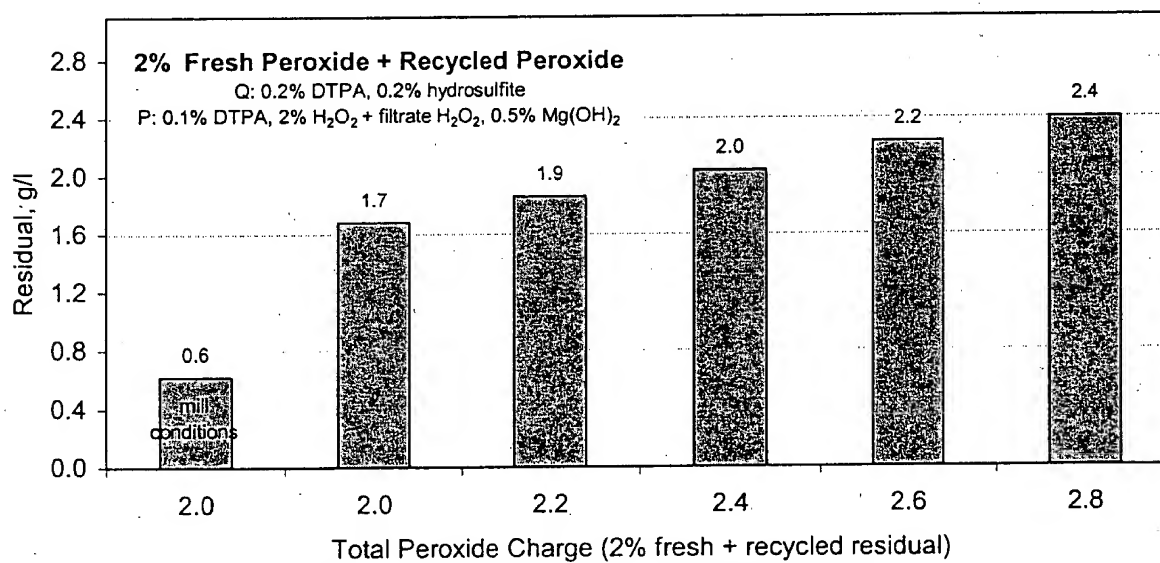


Figure 16. 2% fresh peroxide + residual peroxide – peroxide residual.

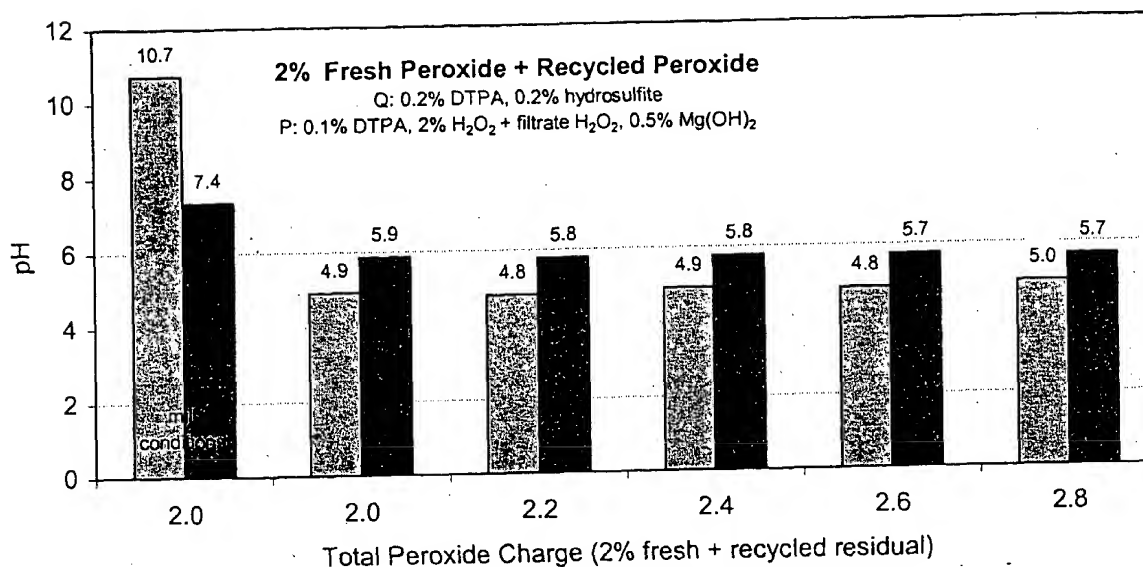


Figure 17. 2% fresh peroxide + residual peroxide – initial and final pH.

For the 1.5% fresh peroxide plus residual peroxide (Figure 18 - Figure 20), the brightness also increases with increasing filtrate peroxide, about a 1.5 brightness point increase with 1% filtrate peroxide added. As with the 2% fresh peroxide, the residual increases, but the percent residual used remains constant.

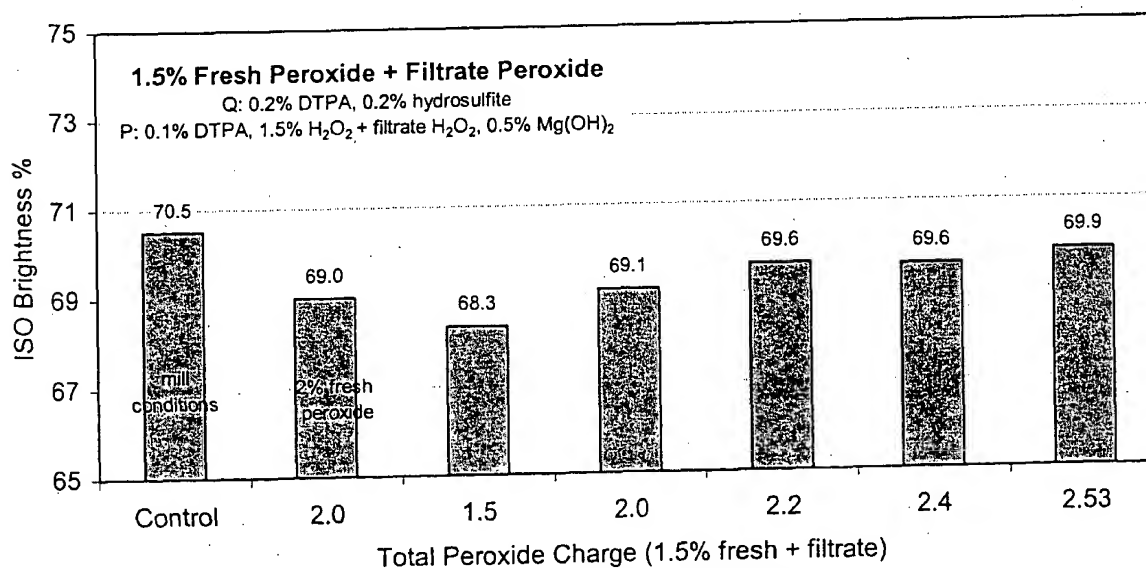


Figure 18. 1.5% fresh peroxide + residual peroxide – brightness.

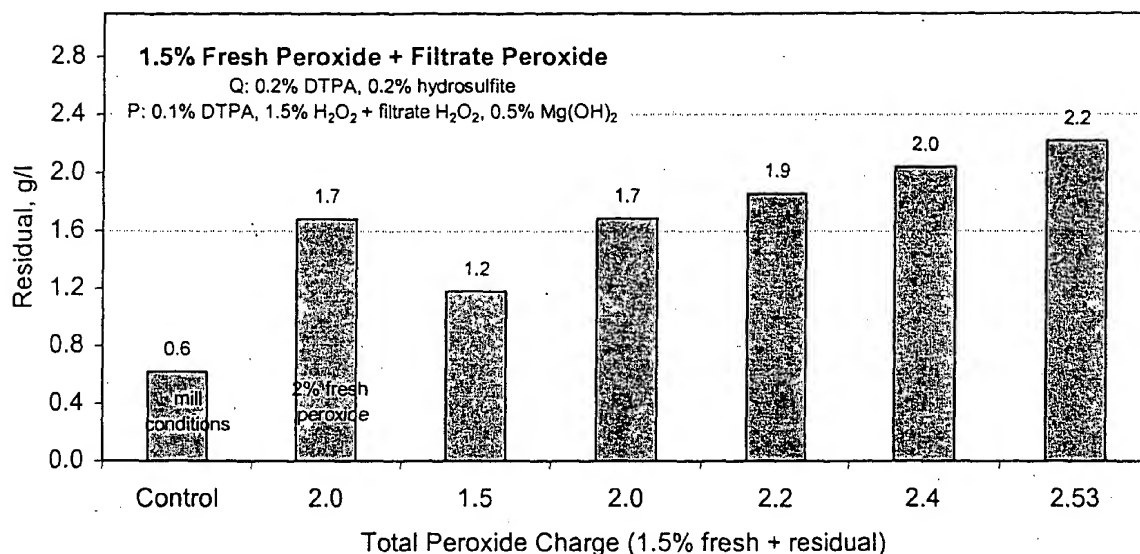


Figure 19. 1.5% fresh peroxide + residual peroxide – peroxide residual.

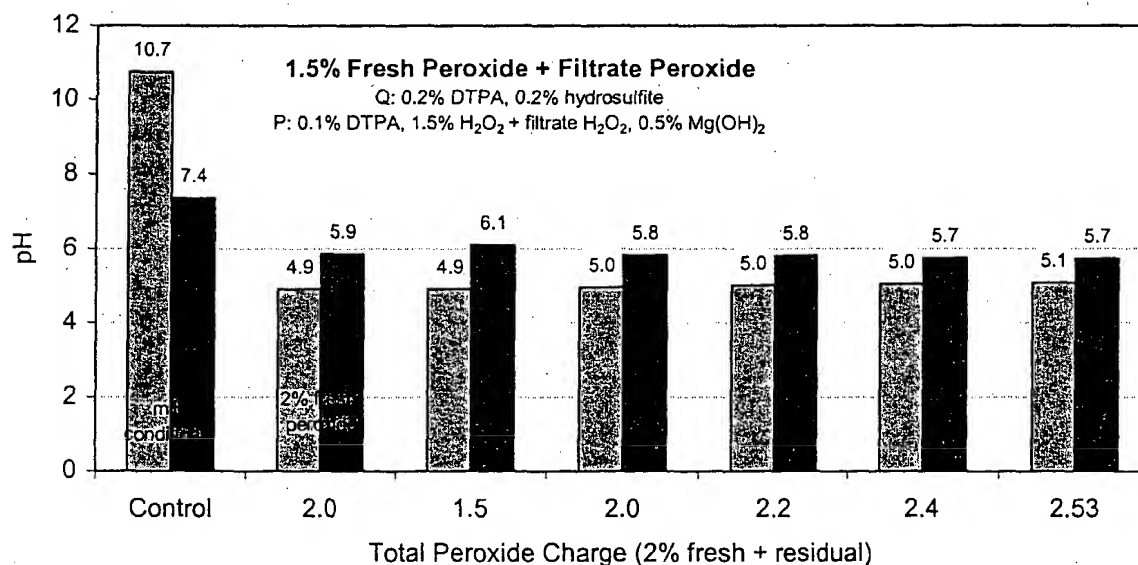


Figure 20. 1.5% fresh peroxide + residual peroxide – initial and final pH.

Figure 21 - Figure 23 compare the responses of the 1.5% and 2% fresh peroxide trials on a total peroxide basis. The response is similar at a given total peroxide, regardless of the level of fresh versus residual peroxide used.



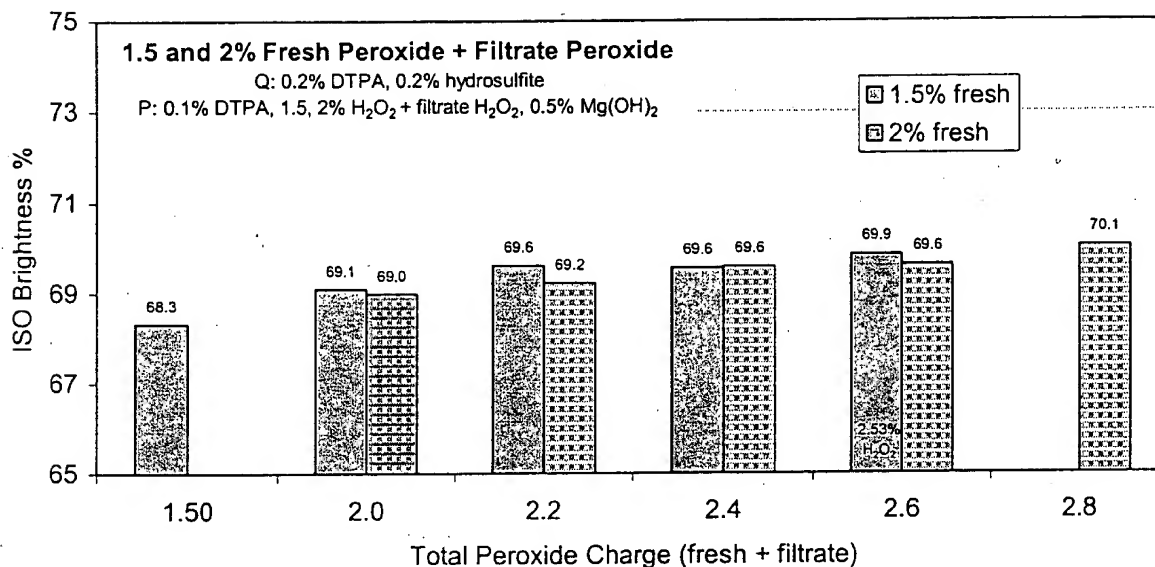


Figure 21. 1.5 and 2% fresh peroxide + residual peroxide – brightness.

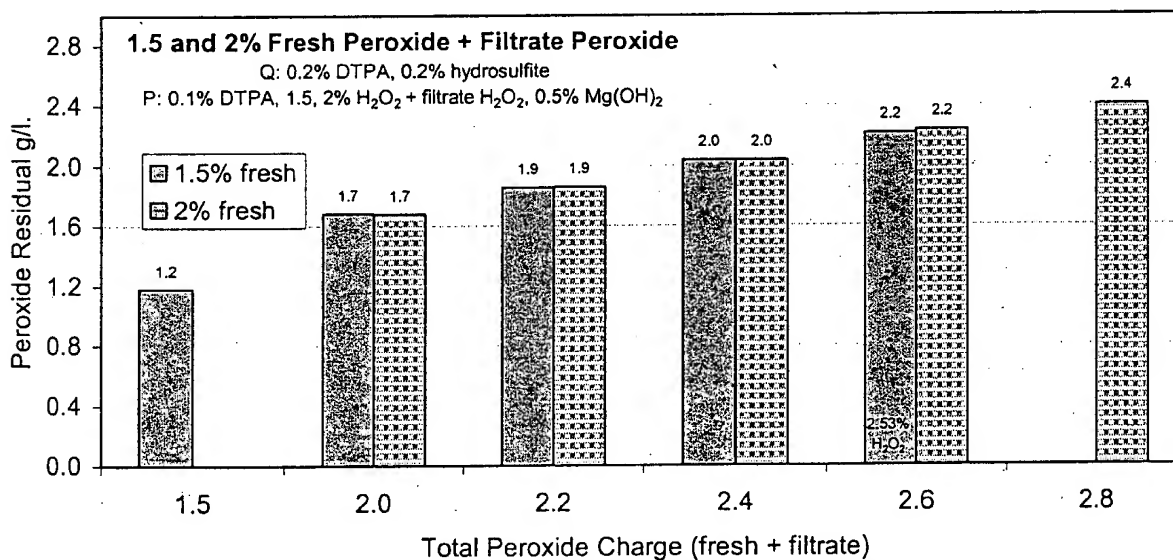


Figure 22. 1.5 and 2% fresh peroxide + residual peroxide – peroxide residual.

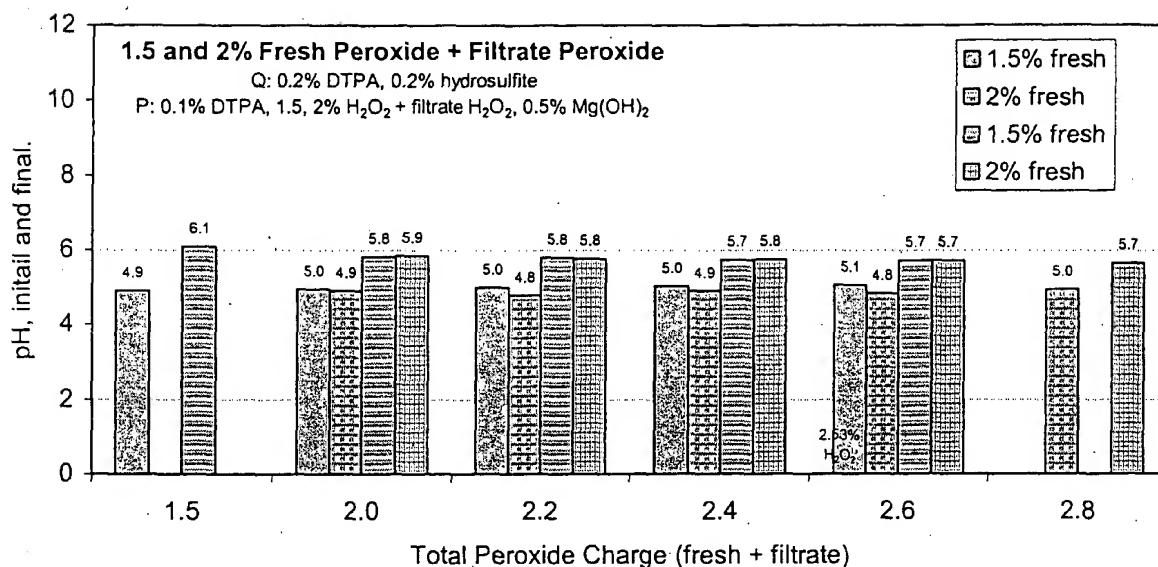


Figure 23. 1.5 and 2% fresh peroxide + residual peroxide – initial and final pH.

The response to additional peroxide from filtrate is less than the response of Champion pulp to additional fresh peroxide in the Phase 1 work. Figure 24 shows the current work and the previous Champion data. The additional fresh peroxide had a much greater impact on the brightness than the current work is showing. However, this was a different pulp.

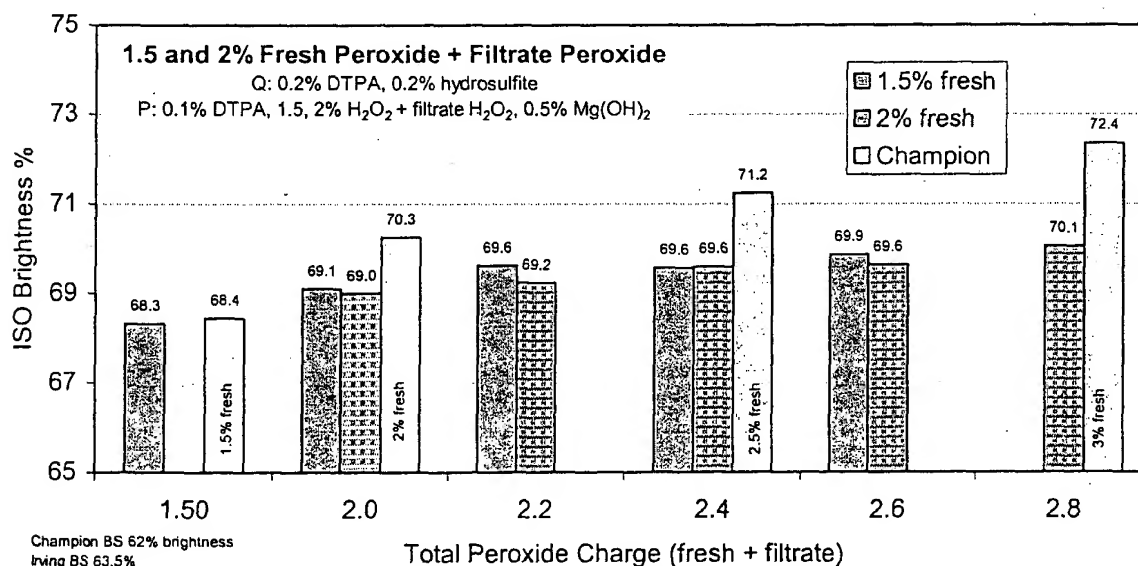


Figure 24. 1.5 and 2% fresh peroxide + residual peroxide, and Champion data – brightness.

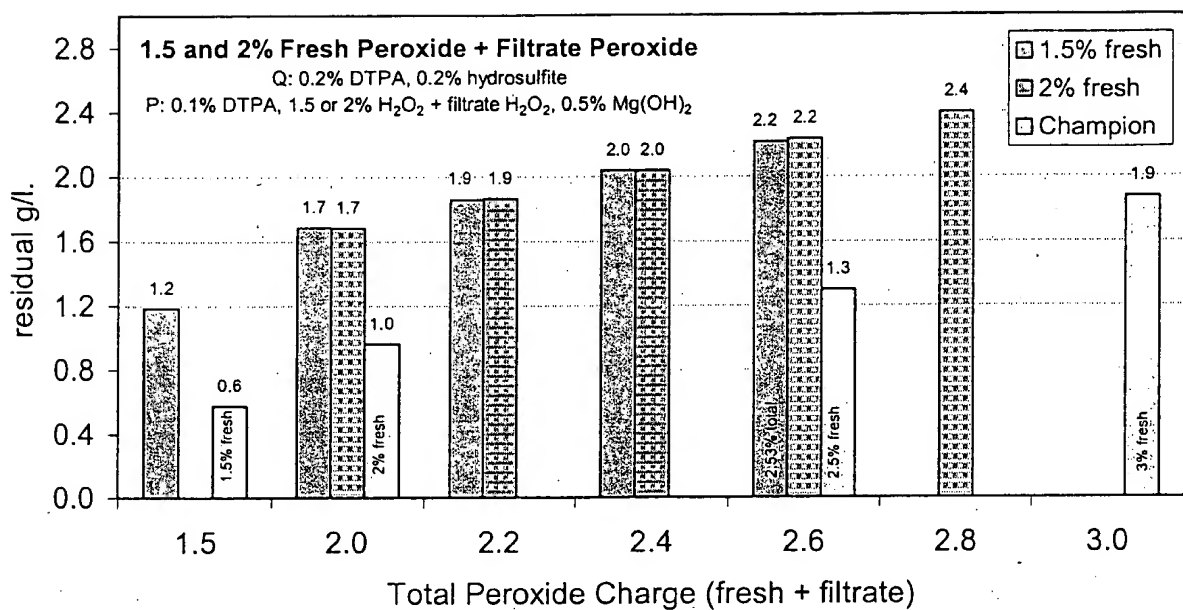


Figure 25

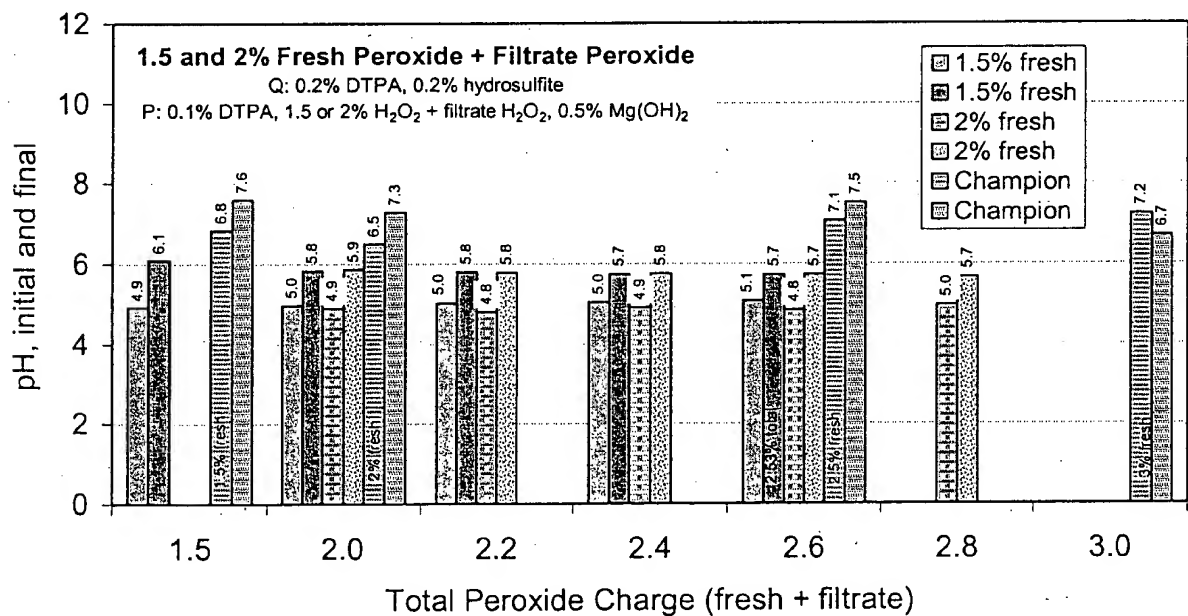


Figure 26

One difference to note in the current experiments is the lower pH. The control, mill condition runs have very similar initial and final pH values to the previous work in Phase 1 on the last pulp

sample, about 10.7 initial to 7.3 final. However, the  $\text{Mg}(\text{OH})_2$  experiments show a difference in the initial pH values. The Phase 1 experiments showed a 5.5 to 6.3 pH range for the initial, and a 6.2 to 6.5 range for the final pH, while the current experiments show a 4.7 to 5.1 range for initial, and a 5.8 to 6.3 range for the final pH. The current experiments have used hydrosulfite in the chelation stage, which may contribute to lower pH. Also, this set of experiments has used the new sample of  $\text{Mg}(\text{OH})_2$  which has a 3.1 micron particle size. In the Phase 1 work, this size did give a lower initial pH, but did not affect brightness results.

Perhaps we need to add additional  $\text{Mg}(\text{OH})_2$  immediately to raise the pH, to get better response.

Figure 27 - Figure 29 show the results of reusing filtrate in consecutive bleaching experiments (using filtrate from experiment 1 in exp 2, then filtrate from exp 2 in exp 3, etc). This showed similar response for all experiments. It seems the measured residual continues to work similarly through several iterations.

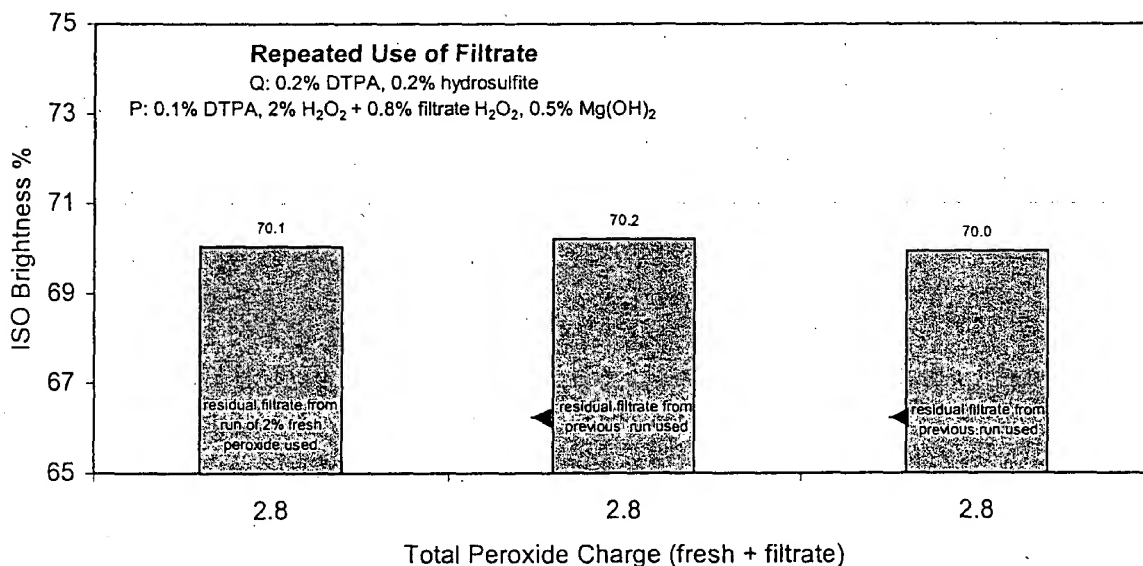


Figure 27. Repeated use of filtrate – brightness.

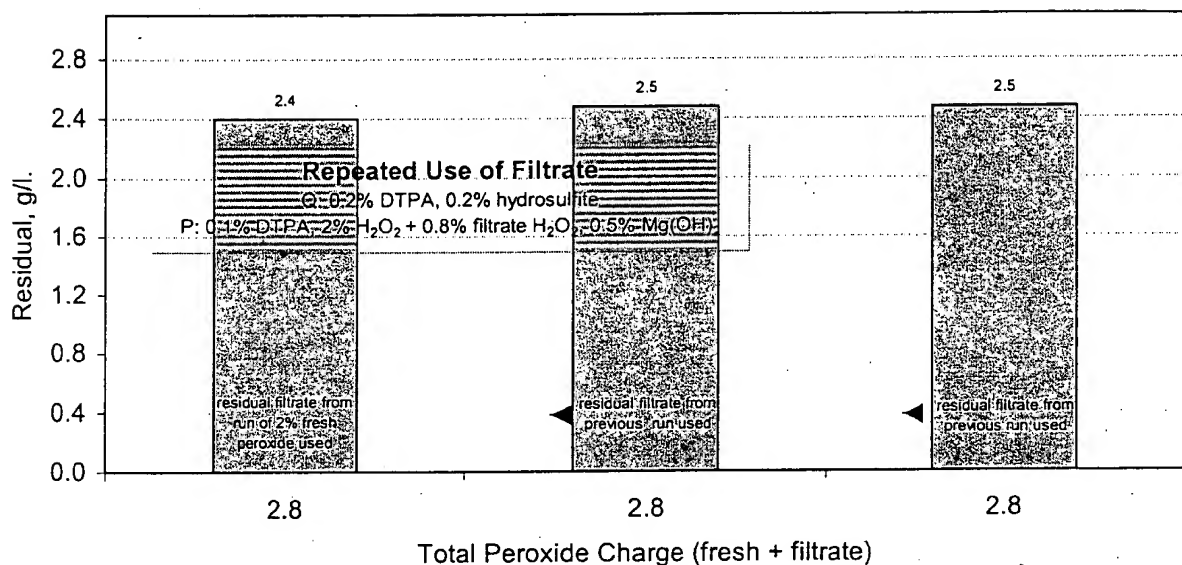


Figure 28. Repeated use of filtrate – peroxide residual.

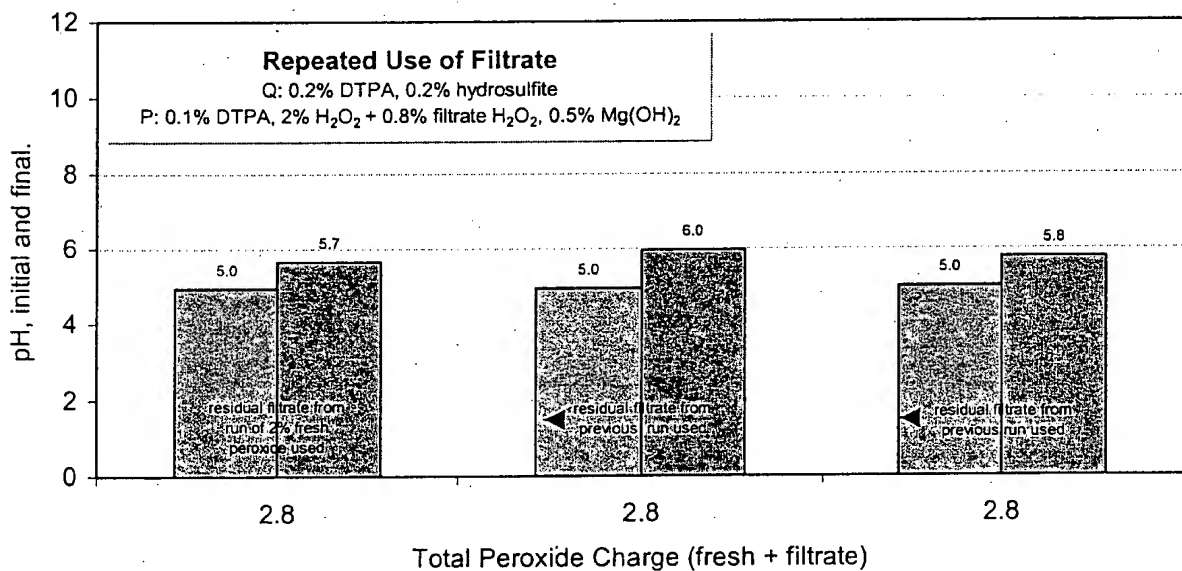


Figure 29. Repeated use of filtrate – initial and final pH.

#### $Mg(OH)_2$ RESPONSE CURVE

The results from the recycled peroxide residual experiments showed a lower brightness gain than might have been expected, perhaps due to a lack of  $Mg(OH)_2$ . Therefore, a response curve

at differing levels of  $\text{Mg}(\text{OH})_2$  was generated, keeping the peroxide charge at 2% and the DTPA in the peroxide stage at 0.1%. Figure 30 - Figure 32 hold the brightness, residual, and pH data, respectively.

$\text{Mg}(\text{OH})_2$  at 1% gave the best brightness result, and exceeded the mill condition control, 71.4 vs. 70.4%. There was still 1.1g/l residual remaining. These results are very close to the split addition results where the total  $\text{Mg}(\text{OH})_2$  was 1%.

Above 1%  $\text{Mg}(\text{OH})_2$ , the brightness begins to drop, and the residual decreases. The pH goes up as more  $\text{Mg}(\text{OH})_2$  is dissolved. We are thinking that these results are due to contaminants in the  $\text{Mg}(\text{OH})_2$ , the ratio of chelant to  $\text{Mg}(\text{OH})_2$  needed, and/or the amount of  $\text{Mg}(\text{OH})_2$  needed to react with the peroxide.

Given that, we are now planning to do two sets of experiments. Since our best result from the current set of data was at 1%  $\text{Mg}(\text{OH})_2$  and 0.1% DTPA, we will repeat the experiment by again varying the  $\text{Mg}(\text{OH})_2$  charge, while also varying the DTPA charge to keep the (1):(0.1)  $\text{Mg}(\text{OH})_2$ :DTPA ratio.

Then, we will continue to keep the peroxide at 2%, but choose the  $\text{Mg}(\text{OH})_2$  charge as 1%. The DTPA: $\text{Mg}(\text{OH})_2$  ratio will be varied, which will give us a DTPA response curve. These experiments are basically part of the third part of the experimental plan, but do need to be done to establish proper reactant ratios.

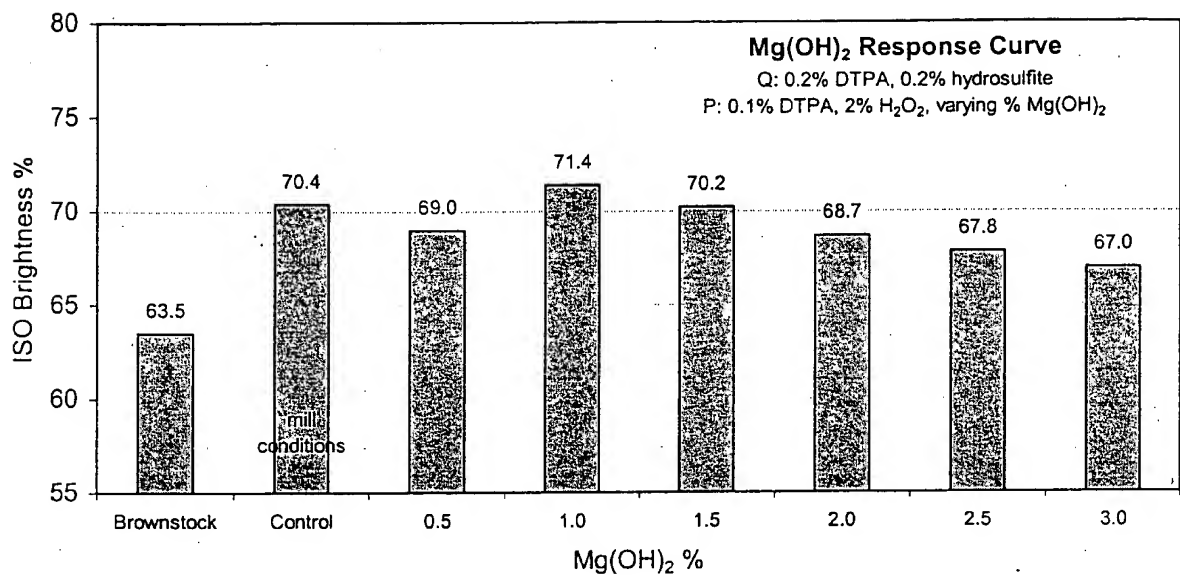


Figure 30. Mg(OH)<sub>2</sub> Response Curve - Brightness.

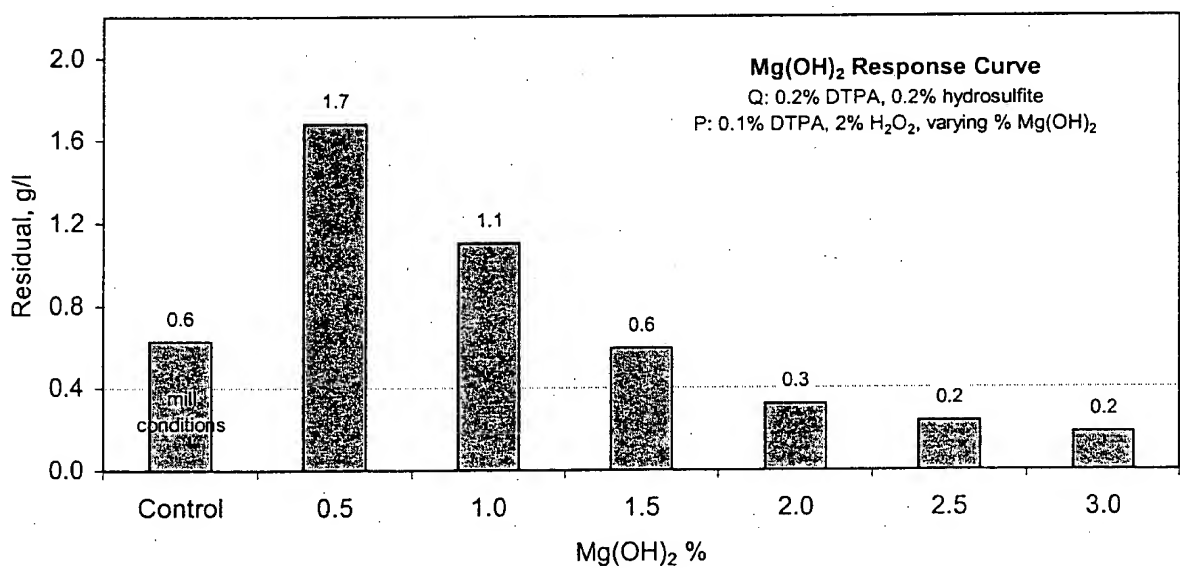


Figure 31. Mg(OH)<sub>2</sub> Response Curve – peroxide residual.

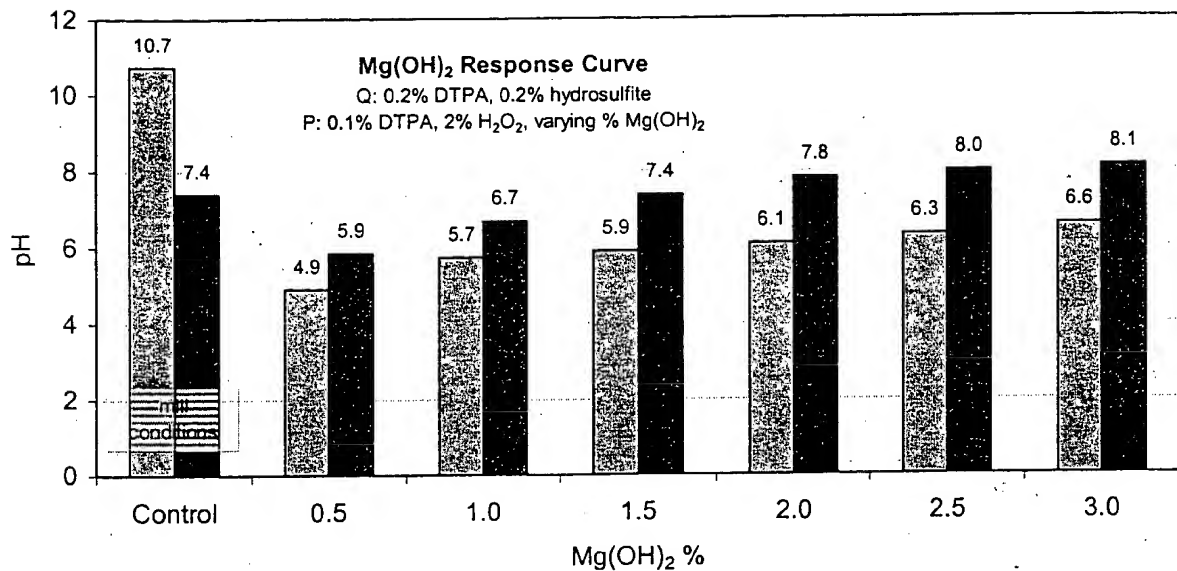


Figure 32. Mg(OH)<sub>2</sub> Response Curve – initial and final pH.

Figure 33, Figure 34, and Figure 35 show previous data re-plotted, split addition Mg(OH)<sub>2</sub> and single dose Mg(OH)<sub>2</sub>, plotted together against total Mg(OH)<sub>2</sub> addition. Where the data sets overlap, brightness values, residuals, and pH values are comparable. This indicates that at the levels of split addition we were using, the total Mg(OH)<sub>2</sub> was the important factor. The experiment should have started with the 1% Mg(OH)<sub>2</sub> level, adding additional Mg(OH)<sub>2</sub> at the split above the 1% level.

The data also indicate that the 1% level is the optimum.



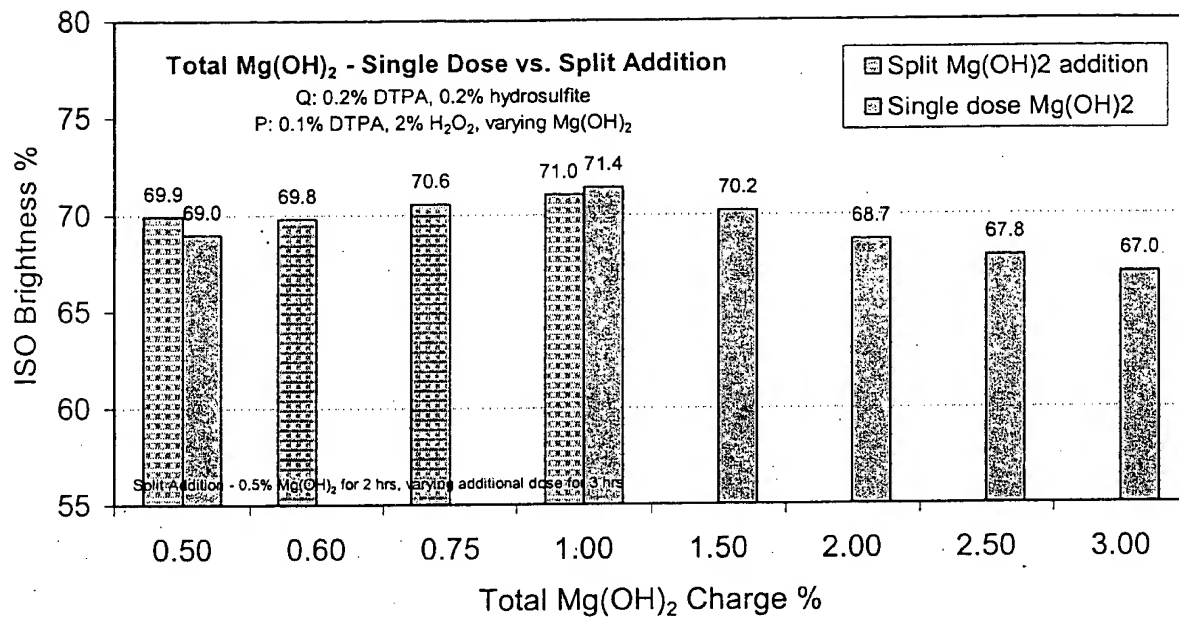


Figure 33. Single Dose Mg(OH)<sub>2</sub> vs. Split Addition – Brightness.

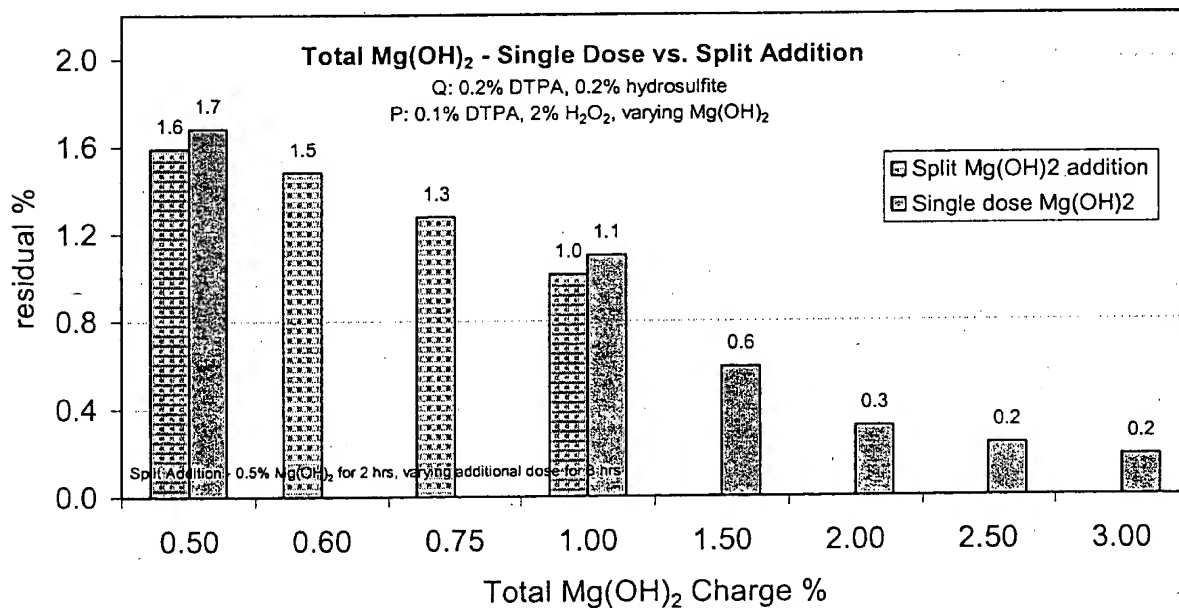


Figure 34. Single Dose Mg(OH)<sub>2</sub> vs. Split Addition – peroxide residual.

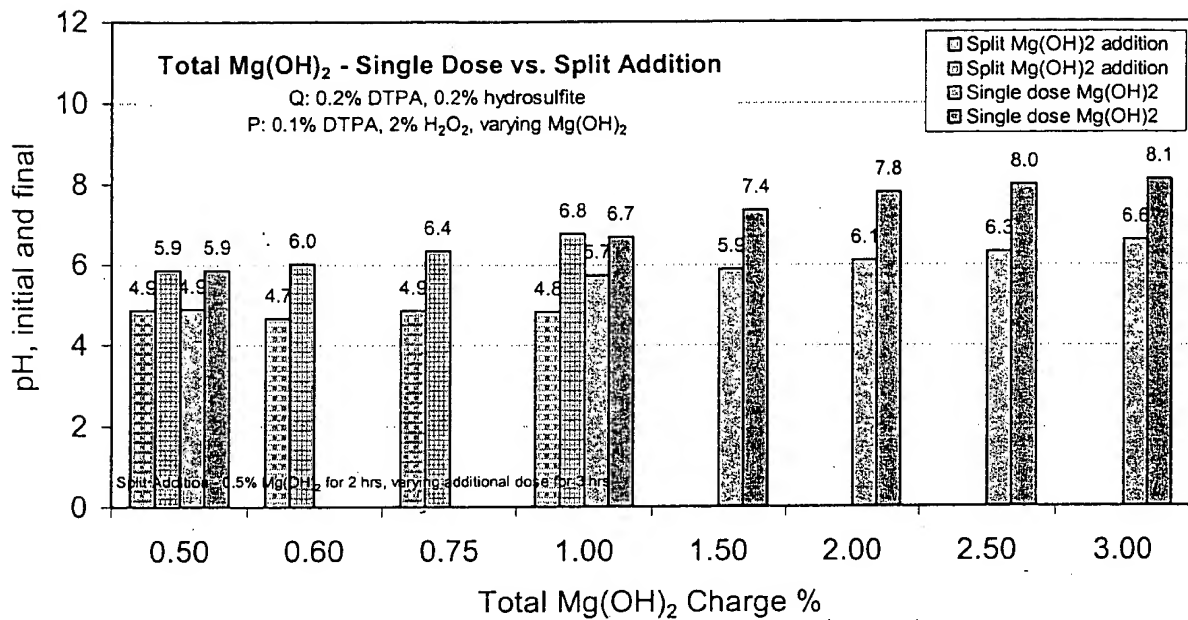


Figure 35. Single Dose Mg(OH)<sub>2</sub> vs. Split Addition – initial and final pH.

#### CHANGING CHELANT RATIOS

##### Constant Chelant:Mg(OH)<sub>2</sub> Ratio

Figure 36, Figure 37 and Figure 38 show constant DTPA:Mg(OH)<sub>2</sub> ratio data, plotted along with the varying ratio data. At the 1 and 1.5% Mg(OH)<sub>2</sub> levels, little difference is seen between the data. At higher Mg(OH)<sub>2</sub> levels, the additional chelant in the constant Mg(OH)<sub>2</sub>:DTPA ratio seems to make some improvement in efficiency of peroxide usage – the brightness goes up, and the residual is higher. However, this level of Mg(OH)<sub>2</sub> is above the optimum brightness value level of 1%.

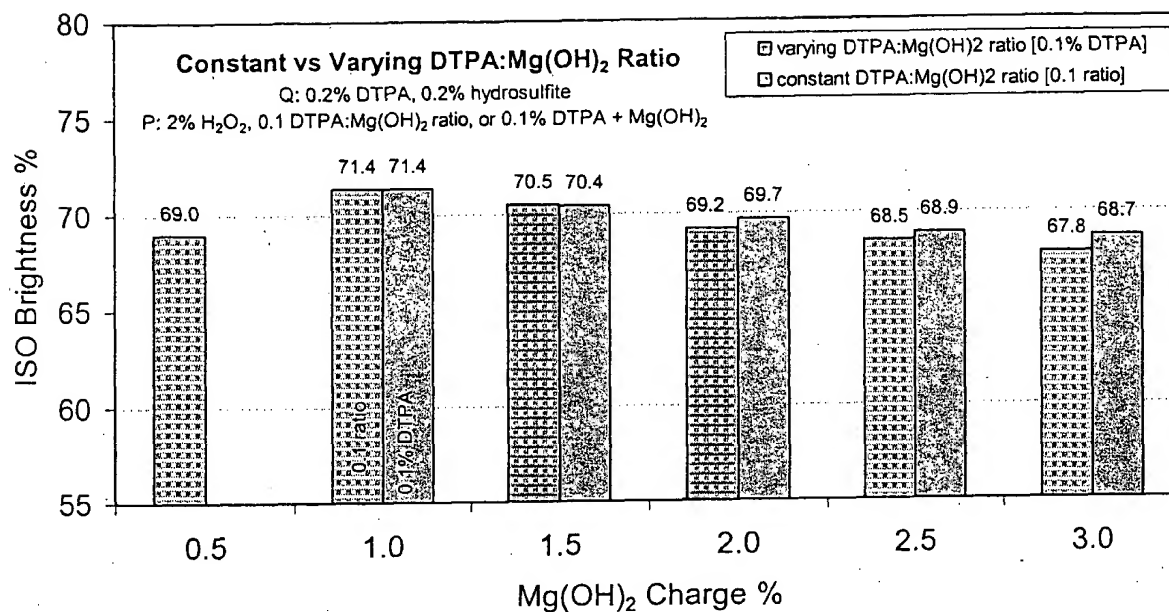


Figure 36. Constant vs. varying DTPA:Mg(OH)<sub>2</sub> ratio – Brightness.

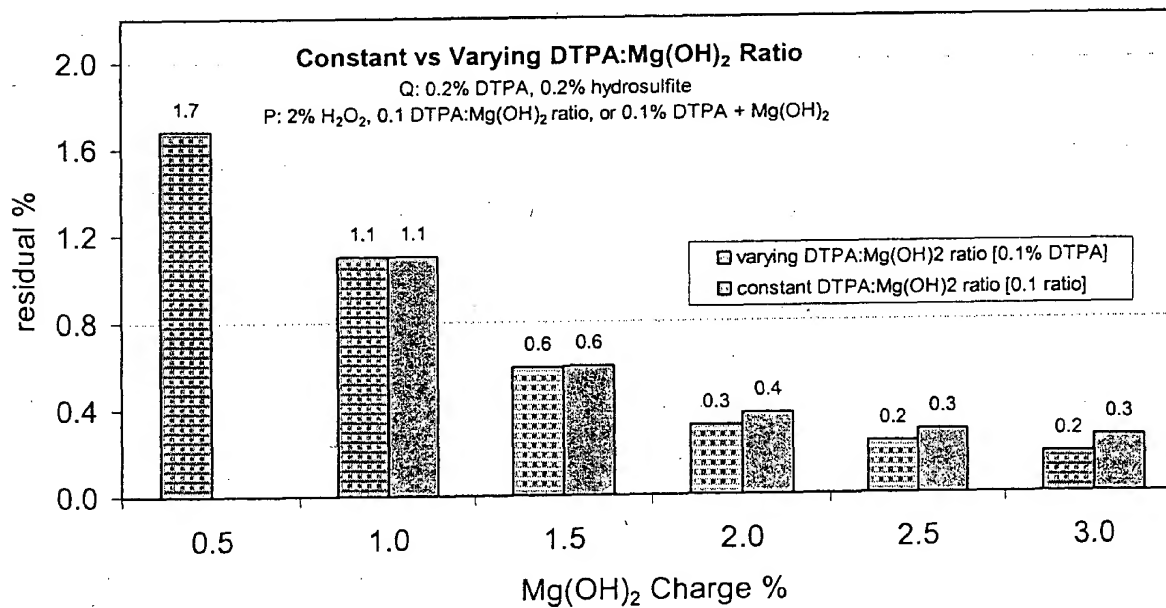


Figure 37. Constant vs. varying DTPA:Mg(OH)<sub>2</sub> ratio – peroxide residual.

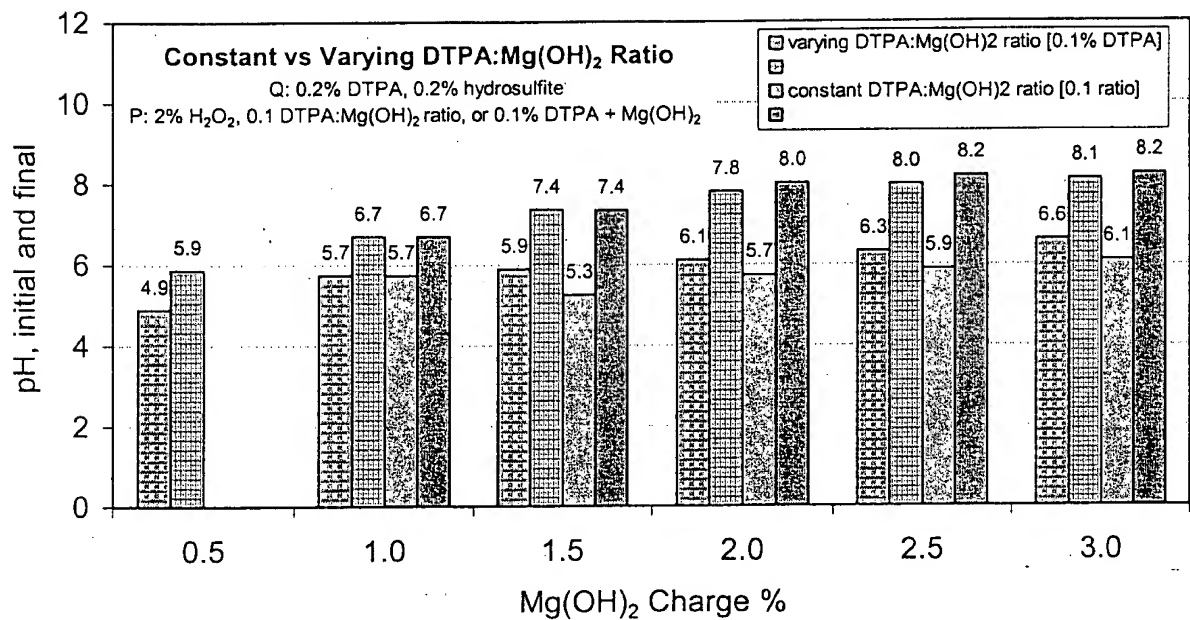


Figure 38. Constant vs. varying DTPA:Mg(OH)<sub>2</sub> ratio – Initial and final pH.

#### Changing Chelant:Mg(OH)<sub>2</sub> Ratio

For this set of experiments, the DTPA:Mg(OH)<sub>2</sub> ratio was increased, by holding the Mg(OH)<sub>2</sub> addition at 1%, and adding more DTPA to the peroxide stage. Figs hold the data. The addition of chelant did not affect the brightness or residual values very much.

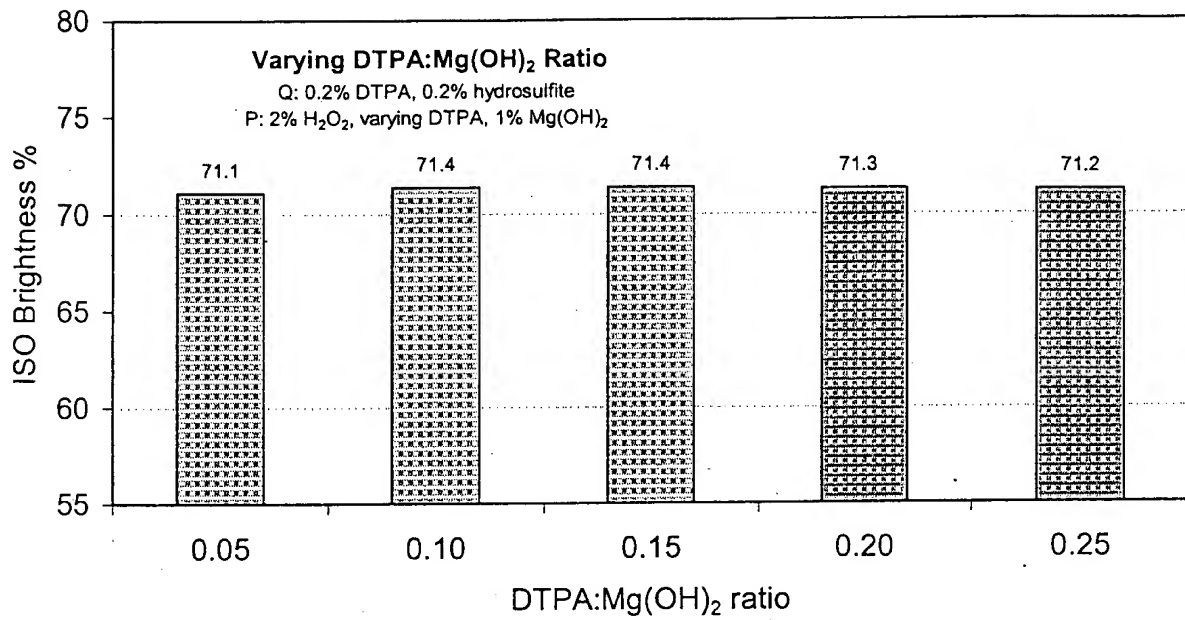


Figure 39. Changing chelant:Mg(OH)<sub>2</sub> ratio, 1% Mg(OH)<sub>2</sub> – brightness.

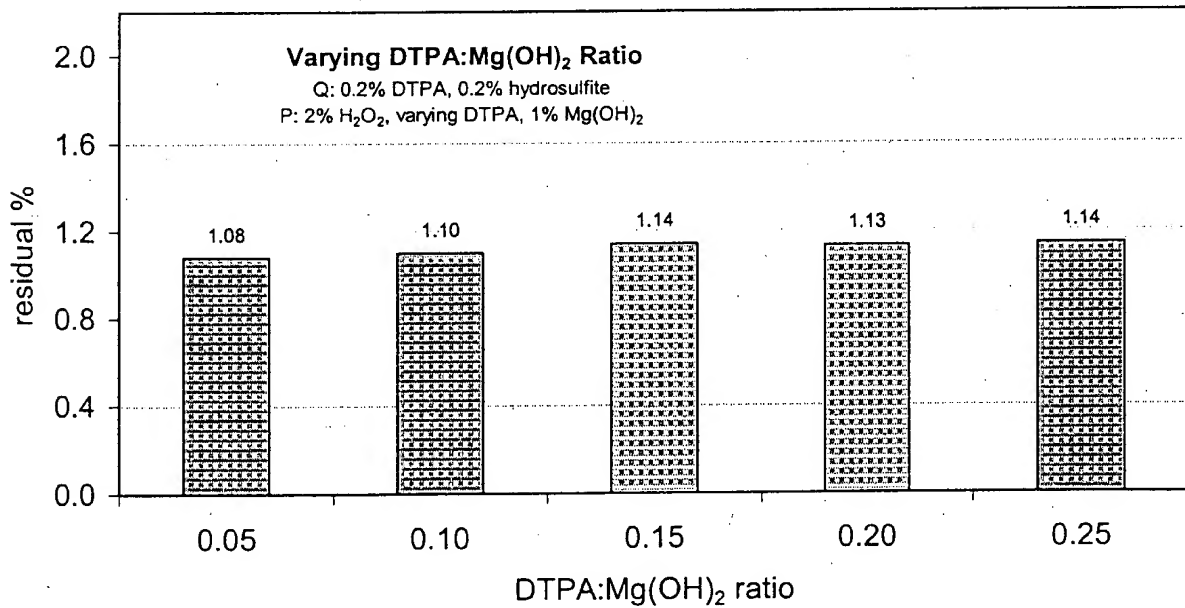


Figure 40. Changing chelant:Mg(OH)<sub>2</sub> ratio, 1% Mg(OH)<sub>2</sub> – Peroxide residual.

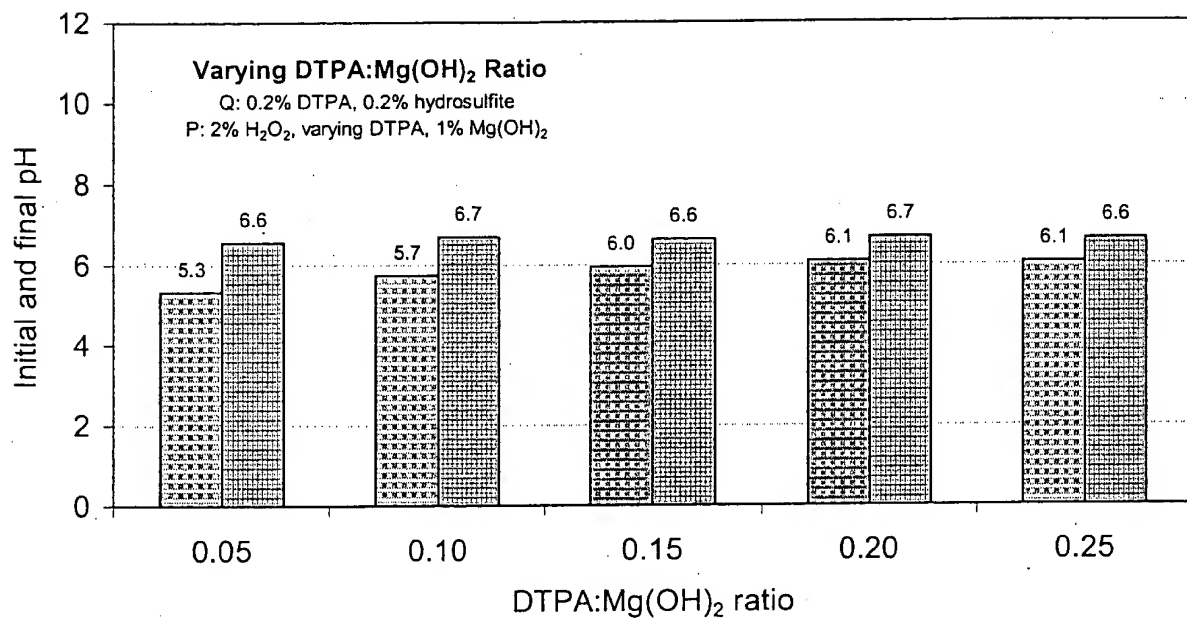


Figure 41. Changing chelant:Mg(OH)<sub>2</sub> ratio, 1% Mg(OH)<sub>2</sub> – Initial and final pH.

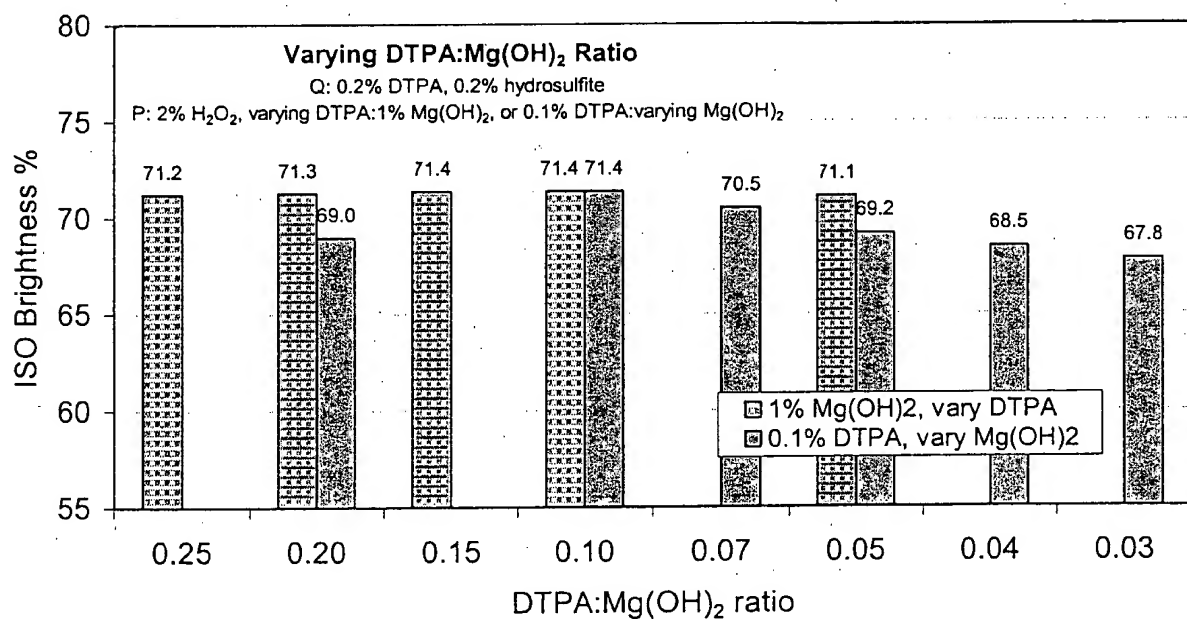


Figure 42. Changing chelant:Mg(OH)<sub>2</sub> ratio, 0.1% DTPA or 1% Mg(OH)<sub>2</sub> – brightness.

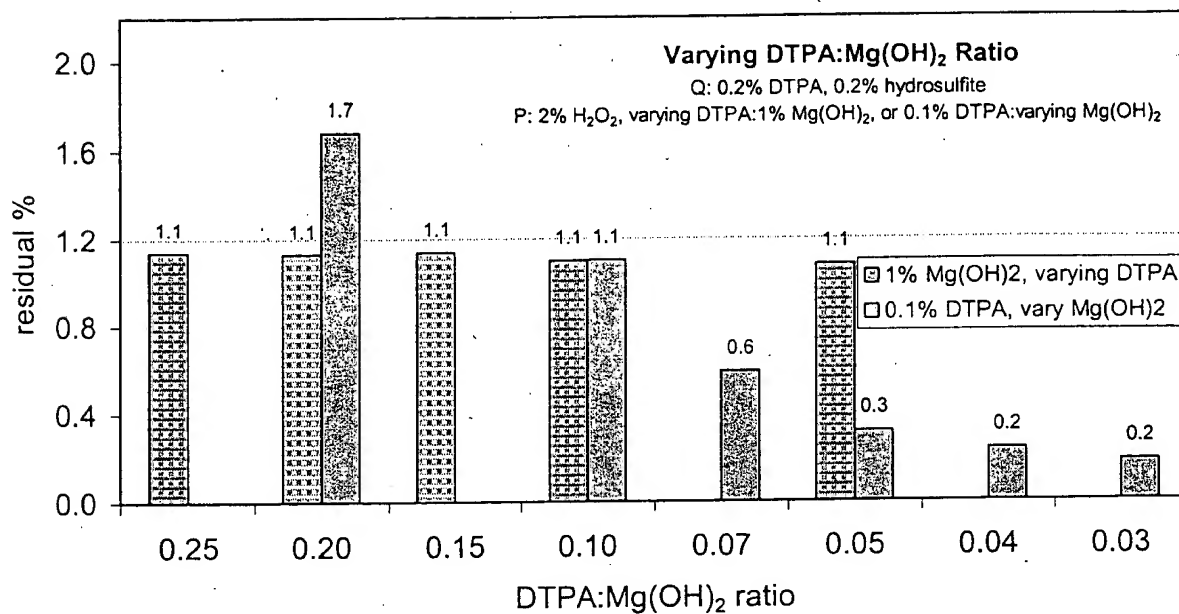


Figure 43. Changing chelant:Mg(OH)<sub>2</sub> ratio, 0.1% DTPA or 1% Mg(OH)<sub>2</sub> – Peroxide residual.

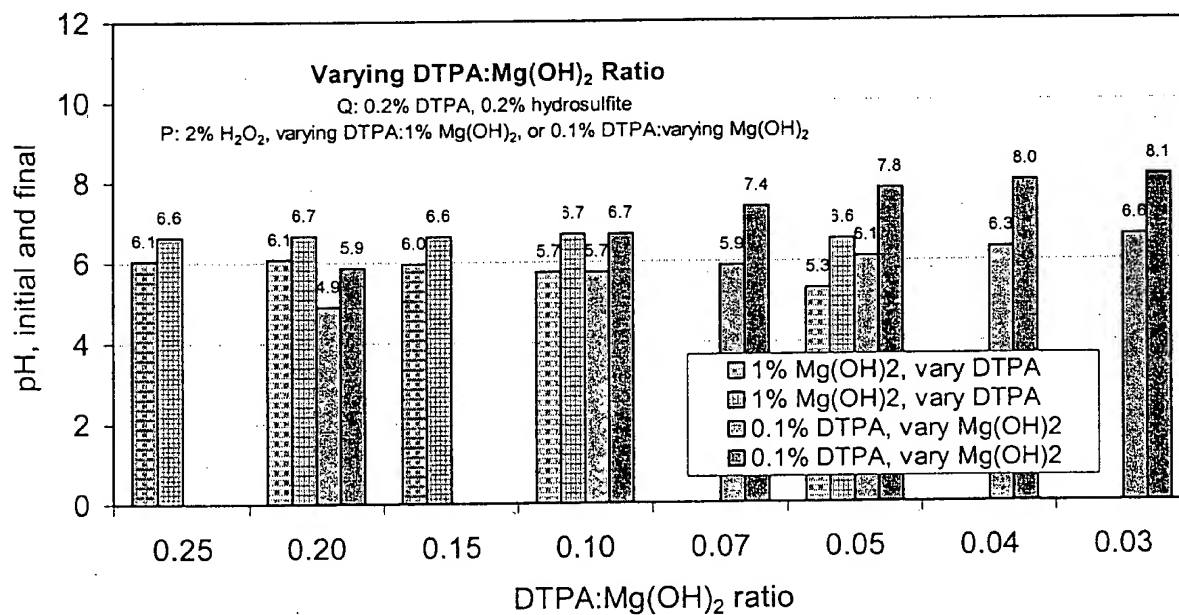


Figure 44. Changing chelant:Mg(OH)<sub>2</sub> ratio, 0.1% DTPA or 1% Mg(OH)<sub>2</sub> – Initial and final pH.

### EFFECTS OF $\text{Mg}(\text{OH})_2$ WITHOUT PEROXIDE

In order to determine the effects of  $\text{Mg}(\text{OH})_2$  on pulp, without peroxide present, a series of experiments were done using no peroxide, while increasing the  $\text{Mg}(\text{OH})_2$  level.

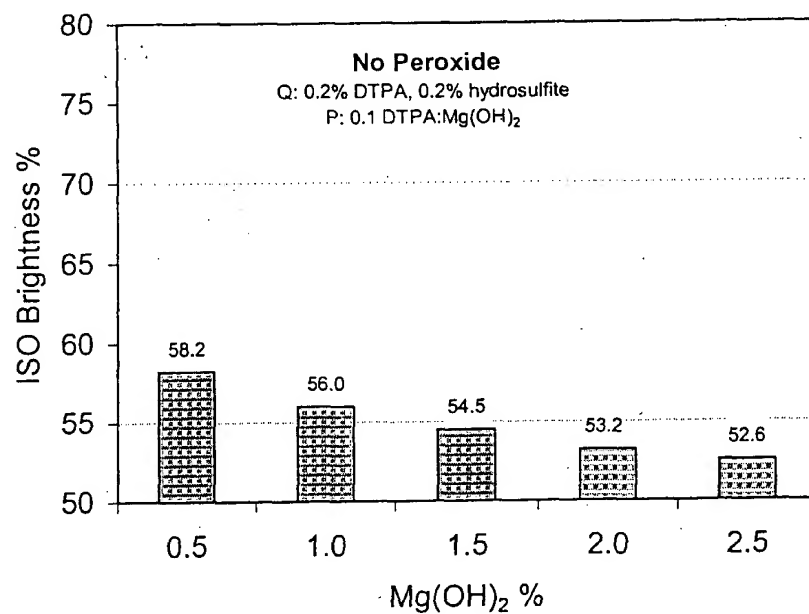


Figure 45. Bleaching with no peroxide – brightness.

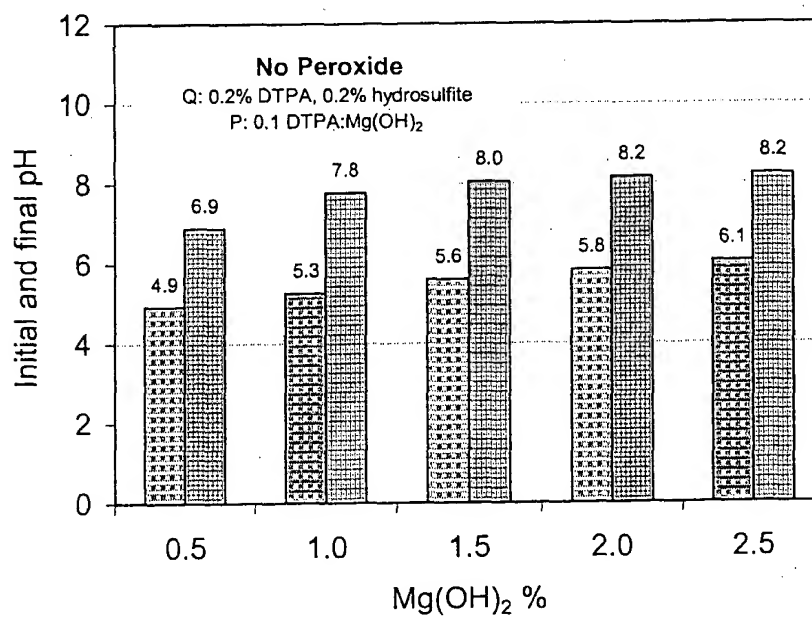


Figure 46. Bleaching with no peroxide – Initial and final pH.



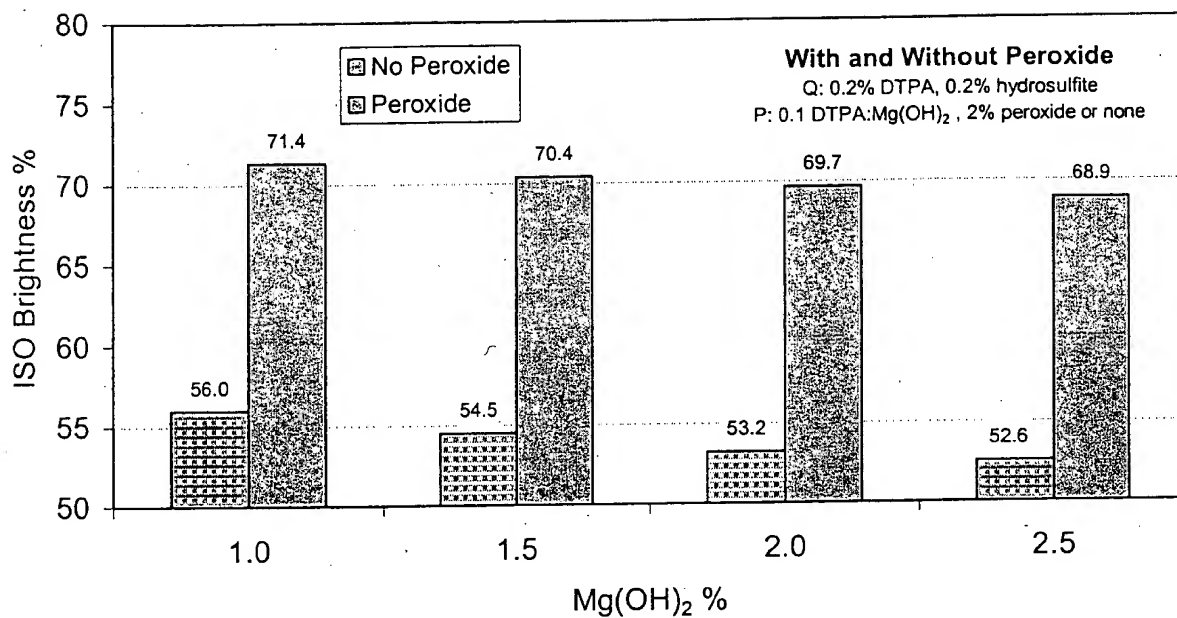


Figure 47. Bleaching with and without peroxide – brightness.

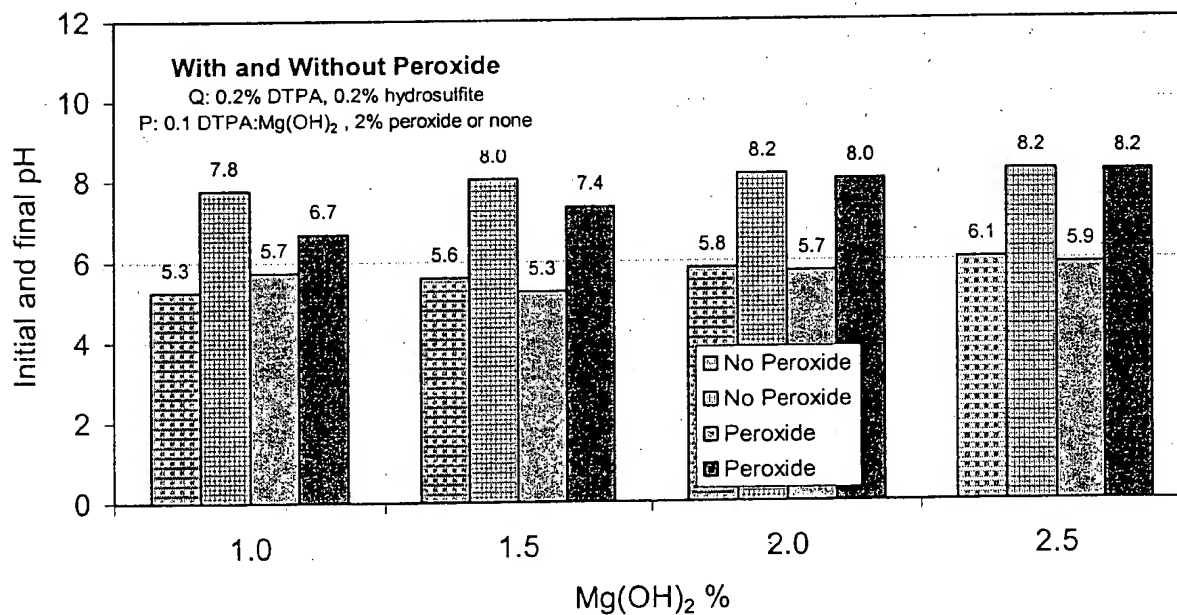


Figure 48. Bleaching with and without peroxide – Initial and final pH.

## EFFECTS OF $Mg(OH)_2$ /PEROXIDE BLEACHING ON COD VALUES

### HANDSHEET STRENGTH VALUES

Handsheets were made from select pulps, to compare strength values for the different pulping conditions. Two control pulps were chosen, and then pulps from various  $Mg(OH)_2$  experiments that had similar brightness values to the control pulps. Figure 49 shows the results of the pulp strength testing of pulps from various experiments, and Table 1 holds the data. Little difference is seen between any of the pulps.

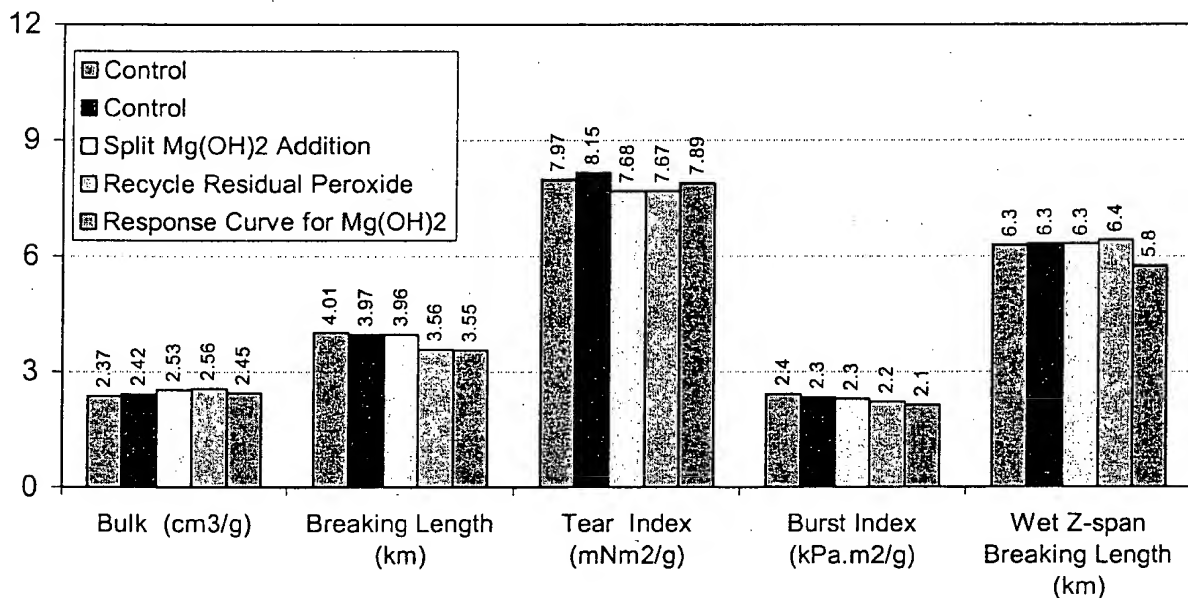


Figure 49. Strength values of handsheets from select pulp samples.

Additional data – latest control, chelant stuff.

**Table 1. Handsheet Strength Data.**

Experiment	Control	Control	Split Mg(OH) <sub>2</sub> Addition	Recycle Residual Peroxide (2% fresh)	Response Curve for Mg(OH) <sub>2</sub>
Brightness	70.51	70.54	70.55	70.06	70.49
Caliper (mm)	0.141	0.141	0.146	0.153	0.154
Sheet Density (g/cm <sup>3</sup> )	0.423	0.414	0.395	0.391	0.409
Bulk (cm <sup>3</sup> /g)	2.37	2.42	2.53	2.56	2.45
grammage (gsm, OD)	59.6	58.4	57.7	59.8	62.9
load (lbf)	8.74	8.46	8.35	7.79	8.16
stretch %	2.61	2.59	2.53	2.39	2.72
integral (lbf-in)	0.62	0.62	0.60	0.51	0.62
Tensile Strength (kN/m)	2.59	2.51	2.48	2.31	2.42
Tensile Index (Nm/g)	39.3	38.9	38.9	35.0	34.8
Breaking Length (km)	4.01	3.97	3.96	3.56	3.55
TEA (J/m <sup>2</sup> )	46.80	46.37	44.99	38.68	46.83
Tear Index (mNm <sup>2</sup> /g)	7.97	8.15	7.68	7.67	7.89
Burst Index (kPa.m <sup>2</sup> /g)	2.41	2.34	2.29	2.21	2.13
Wet Z-span Breaking Length (km)	6.3	6.3	6.3	6.4	5.8

**BRIGHTNESS REVERSION**

Results from previous Champion and Irving pulps.

**Table 2. Brightness reversion for Mg(OH)<sub>2</sub> and MgO pulp samples.**

	Brightness, ISO %		Brightness Reversion	%
	Initial	After aging		
Control 2hr (D2)	70.8	66.7	4.1	5.8
Mg(OH) <sub>2</sub> 2 hr (F3)	69.2	64.8	4.4	6.4
MgO 2 hr	70.5	65.9	4.6	6.5
Control 5 hr	70.0	66.7	3.3	4.7
Mg(OH) <sub>2</sub> 5 hr (f-1)	68.4	64.7	3.7	5.4
MgO 2 hr	69.4	66.6	2.8	4.0

Do test on same pulps as HS?

**METALS ANALYSIS/ASH CHEMISTRY**

Will be done for same pulps as HS.

Table 3. Chemical and physical analysis of magnesium hydroxide samples (provided by Martin Marietta).

Sample	Particle Size ( $\mu\text{m}$ )	Surface Area ( $\text{m}^2/\text{g}$ )	% Solids	Viscosity (cps)	Mg(OH) <sub>2</sub> <sup>1</sup> (%)	Ca O (%)	SiO <sub>2</sub> (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	Al <sub>2</sub> O <sub>3</sub> (%)	SO <sub>3</sub> (%)	Cl <sup>-</sup> (%)	Mn (ppm)	LOI (%)
<b>D Reactor Slurries:</b>													
P277-261-1	2.50	10.4	59.8	135	98.71	0.67	0.19	0.09	0.06	0.04	0.23	100.0	~31.0
P277-261-2	1.52	11.4	59.8	180	98.72	0.67	0.19	0.09	0.06	0.03	0.23	106.0	~31.0
P277-261-3	0.65	13.6	59.8	205	98.74	0.67	0.19	0.09	0.06	0.01	0.23	112.0	~31.0
<b>C Reactor Slurries:</b>													
P277-262-1	0.415	22.3	53.4	2840	98.74	0.64	0.19	0.10	0.06	0.01	0.25	~100.0	~31.0
P277-262-2	0.603	18.4	56.4	8450	98.73	0.65	0.19	0.09	0.06	0.01	0.26	~100.0	~31.0
P277-262-3	1.461	16.8	56.4	830	98.75	0.64	0.19	0.09	0.06	0.01	0.25	~100.0	~31.0
P277-262-4	3.101	15.5	56.4	200	98.74	0.64	0.19	0.09	0.06	0.01	0.26	~100.0	~31.0

<sup>1</sup> Mg(OH)<sub>2</sub> % by difference (dry basis).

<sup>2</sup> May represent agglomeration of colloidal particles and not individual particles.

NT = not tested

## CONCLUSIONS

## APPENDIX

APPENDIX A – BLEACHING RESULTS, JANUARY IRVING PULP SAMPLE

Table 4. Bleaching Results – Control and Split  $Mg(OH)_2$  Addition

		exp. time, Date	% $Na_2O$	% $HOZ$	Q stage DTPA %	P stage DTPA %	total DTPA %	$H_2O_2$ fresh %	$H_2O_2$ filtrate %	total $H_2O_2$ %	$Mg(OH)_2$ %	$H_2O_2$ $Mg(OH)_2$	P stage DTPA: $Mg(OH)_2$	Initial pH	Final pH	Residual $H_2O_2$ (g/l)	% $H_2O_2$ consumed	% $H_2O_2$ / point br gain	Brightn ess % ISO	L	a	b	COD (mg/l)
	Brownstock	1/11																					
Control	Q & P stages consecutive days	5	3	1.5	0.3		0.3	2.0		2.0				10.71	7.59	0.65	71	10.1	70.51	88.7	0.17	12.62	
		5	3	1.5	0.3		0.3	2.0		2.0				10.76	7.32	0.59	73	10.4	70.54	92.5	-1.51	12.20	7400
		5	3	1.5	0.3		0.3	2.0		2.0				10.74	7.21	0.63	72	10.1	70.58	92.6	-1.61	12.25	7410
		5	3	1.5	0.3		0.3	2.0		2.0				10.72	7.54	0.65	71	11.2	69.86	92.7	-1.48	12.46	7320
		5/2	3	1.5	0.3		0.3	2.0		2.0				10.77	7.40	0.71	68	9.4	70.76	92.2	-1.43	12.31	7220
Split $Mg(OH)_2$ addition	Q & P stages same day	5	3	1.5	0.3		0.3	2.0		2.0				10.76	7.30	0.63	72	10.4	70.39	92.6	-1.47	12.35	7370
	AVERAGE	5	3	1.5	0.3		0.3	2.0		2.0				10.74	7.39	0.64	71	10.3	70.44	92.5	-1.54	12.29	7344
	Q & P stages consecutive days	2/3			0.2	0.1	0.30	2.0		2.0	0.5/0		0.20	4.86	5.86	1.59	28	4.3	69.92	92.1	-1.22	12.16	4430
		2/3			0.2	0.1	0.30	2.0		2.0	0.5/0.1		0.17	4.66	6.03	1.48	33	5.2	69.81	92.1	-1.12	12.27	4100
		2/3			0.2	0.1	0.30	2.0		2.0	0.5/0.25		0.13	4.86	6.35	1.28	42	6.0	70.55	92.7	-1.59	12.43	4350
	Q & P stages same day	2/3			0.2	0.1	0.30	2.0		2.0	0.5/0.5		0.10	4.83	6.78	1.01	54	7.2	71.04	92.9	-1.73	12.28	5060
		2/3			0.2	0.1	0.30	2.0		2.0	0.5/0.25		0.13	5.03	6.41	1.31	41	5.9	70.47	92.6	-1.31	12.37	4300

Table 5. Bleaching Results – Recycling Residual Peroxide.

		exp. Date	time, hours	% $\text{Na}_2\text{SiO}_3$	% $\text{NaOH}$	Q stage* DTPA %	P stage DTPA %	total DTPA %	$\text{H}_2\text{O}_2$ fresh %	$\text{H}_2\text{O}_2$ filtrate %	total $\text{H}_2\text{O}_2$ %	$\text{Mg}(\text{OH})_2$ %	$\text{H}_2\text{O}_2$ : $\text{Mg}(\text{OH})_2$	P stage DTPA: $\text{Mg}(\text{OH})_2$	Initial pH	Final pH	Residual $\text{H}_2\text{O}_2$ (g/l)	% $\text{H}_2\text{O}_2$ consumed	% $\text{H}_2\text{O}_2$ / point brighten gain	Brightness % ISO	L	a	b	COD (mg/l)	
		Brownstock	1/11								10									63.53	88.7	0.17	12.62		
Recycle Residual Peroxide		obtain residual	5			0.2	0.1	0.30	2.0		2.0	0.50	4.0	0.2	5.01	5.85	1.64	26	4.7	68.97	91.8	-1.14	12.46	4050	
	5				0.2	0.1	0.30	2.0		2.0	0.50	4.0	0.2	4.76	5.85	1.68	24	4.7	68.58	91.7	-1.17	12.54	4010		
	5				0.2	0.1	0.30	2.0		2.0	0.50	4.0	0.2	4.73	5.80	1.70	23	4.2	68.94	91.9	-1.18	12.59	4010		
	5				0.2	0.1	0.30	2.0		2.0	0.50	4.0	0.2	4.91	5.88	1.71	22	4.0	69.15	91.9	-1.21	12.46	3900		
	5				0.2	0.1	0.30	2.0		2.0	0.50	4.0	0.2	4.78	5.85	1.70	23	4.0	69.23	92.0	-1.37	12.50			
			5			0.2	0.1	0.30	2.0		2.0	0.50	4.0	0.2	5.20	5.94	1.67	24	4.4	69.08	92.0	-1.27	12.56		
			5*			0.2	0.1	0.30	2.0		2.0	0.50	4.0	0.2	4.96	5.95	1.65	25	4.3	69.40	91.9	-1.10	12.27	3540	
		AVERAGE		5 <sup>(a)</sup>		0.2	0.1	0.30	2.0		2.0	0.50	4.0	0.2	4.90	5.86	1.68	24	4.3	68.99	91.9	-1.22	12.52	3993	
		2% fresh, add filtrate to target brightness [A]		5		0.2	0.1	0.30	2.0	0.2	0.2	2.2	0.50	4.4	0.2	4.80	5.78	1.86	24	4.2	69.23	91.9	-1.12	12.33	4350
			5			0.2	0.1	0.30	2.0	0.4	0.4	2.4	0.50	4.8	0.2	4.90	5.76	2.04	24	3.9	69.60	92.2	-1.22	12.50	4610
		5			0.2	0.1	0.30	2.0	0.6	0.6	2.6	0.50	5.2	0.2	4.84	5.72	2.24	23	3.7	69.64	92.3	-1.23	12.52	5040	
		5			0.2	0.1	0.30	2.0	0.8	0.8	2.8	0.50	5.6	0.2	4.96	5.67	2.40	23	3.5	70.06	92.4	-1.30	12.33	4350	
	1.5% fresh, add residual to target brightness [B]		5		0.2	0.10	0.30	1.5	0.0	0.0	1.5	0.50	3.0	0.2	4.91	6.09	1.18	29	6.1	68.33	91.5	-1.11	12.48	3940	
		5			0.2	0.10	0.30	1.5	0.5	0.5	2.0	0.50	4.0	0.2	4.96	5.83	1.69	23	4.2	69.10	92.0	-1.23	12.58	4520	
		5			0.2	0.10	0.30	1.5	0.7	0.7	2.2	0.50	4.4	0.2	5.01	5.80	1.86	23	3.7	69.62	92.0	-1.57	12.18	4910	
		5			0.2	0.10	0.30	1.5	0.9	0.9	2.4	0.50	4.8	0.2	5.04	5.74	2.04	24	3.9	69.57	92.0	-1.58	12.22	5150	
		5			0.2	0.10	0.30	1.5	1.03	1.03	2.53	0.50	5.1	0.2	5.07	5.72	2.22	21	3.3	69.86	92.3	-1.39	12.44	5560	
	reuse residual from previous run [C]		5		0.2	0.1	0.30	2.0	0.8	0.8	2.8	0.50	5.6	0.2	4.96	5.97	2.48	20	3.0	70.22	92.4	-1.38	12.29	5480	
		5			0.2	0.1	0.30	2.0	0.8	0.8	2.8	0.50	5.6	0.2	5.00	5.77	2.48	20	3.2	69.95	92.2	-1.59	12.20	5100	

Table 6. Bleaching Results – Chelant Ratios.

		exp. time, Date	% Na <sub>2</sub> SiO <sub>3</sub>	% NaOH	Q stage* DTPA %	P stage DTPA %	total DTPA %	H <sub>2</sub> O <sub>2</sub> fresh %	H <sub>2</sub> O <sub>2</sub> filtrate %	total H <sub>2</sub> O <sub>2</sub> %	Mg(OH) <sub>2</sub> %	H <sub>2</sub> O <sub>2</sub> : Mg(OH) <sub>2</sub>	P stage DTPA: Mg(OH) <sub>2</sub>	Initial pH	Final pH	Residual H <sub>2</sub> O <sub>2</sub> (g/l)	% H <sub>2</sub> O <sub>2</sub> consumed	% H <sub>2</sub> O <sub>2</sub> / point brighten gain	Brightness % ISO	L	a	b	COD (mg/l)	
	Brownstock	1/11								0									63.53	88.7	0.17	12.62		
response curve for Mg(OH) <sub>2</sub>		4/20	5 <sup>(a)</sup>		0.2	0.1	0.30	2.0		2.0	0.5	4.0	0.2	4.90	5.86	1.68	24	4.3		68.99	91.9	-1.22	12.52	3993
	changing ratio of H <sub>2</sub> O <sub>2</sub> to Mg(OH) <sub>2</sub>		5 <sup>(b)</sup>		0.2	0.1	0.30	2.0		2.0	1.0	2.0	0.10	5.74	6.69	1.10	50	6.4		71.37	73.0	-1.77	12.15	4490
			5		0.2	0.1	0.30	2.0		2.0	1.5	1.3	0.07	5.90	7.37	0.59	73	10.5		70.49	92.6	-1.76	12.47	5110
			5		0.2	0.1	0.30	2.0		2.0	2.0	1.0	0.05	6.10	7.81	0.32	85	15.1		69.18	91.9	-1.71	12.69	5270
			5		0.2	0.1	0.30	2.0		2.0	2.0	2.5	0.8	6.32	7.98	0.24	89	18.0		68.48	91.6	-1.72	13.00	5280
Optimize Chelant Dosage			5		0.2	0.1	0.30	2.0		2.0	3.0	0.7	0.03	6.60	8.10	0.18	92	21.5		67.80	91.4	-1.79	13.38	5260
	constant DTPA: Mg(OH) <sub>2</sub> ratio	4/27	5 <sup>(b)</sup>		0.2	0.1	0.30	2.0		2.0	1.0	2.0	0.10	5.74	6.69	1.10	50	6.4		71.37	93.0	-1.77	12.15	4490
			5		0.2	0.15	0.35	2.0		2.0	1.5	1.33	0.10	5.26	7.35	0.60	73	10.6		70.42	92.8	-1.76	12.55	5190
			5		0.2	0.20	0.40	2.0		2.0	2.0	1.00	0.10	5.74	8.02	0.37	83	13.5		69.67	92.3	-1.76	12.47	5380
			5		0.2	0.25	0.45	2.0		2.0	2.0	2.5	0.80	5.90	8.19	0.29	87	16.2		68.89	92.0	-1.70	12.75	5400
Optimize Chelant Dosage			5		0.2	0.30	0.50	2.0		2.0	3.0	0.67	0.10	6.10	8.24	0.26	88	17.1		68.68	92.0	-1.77	12.85	5870
	differing DTPA: Mg(OH) <sub>2</sub> ratio	5/2	5		0.2	0.05	0.25	2.0		2.0	1.0	2.0	0.05	5.32	6.55	1.08	51	6.7		71.09	92.8	-1.79	12.17	4520
			5 <sup>(b)</sup>		0.2	0.1	0.30	2.0		2.0	1.0	2.0	0.10	5.74	6.69	1.10	50	6.4		71.37	93.0	-1.77	12.15	4490
			5		0.2	0.15	0.35	2.0		2.0	1.0	2.0	0.15	5.95	6.63	1.14	48	6.1		71.38	93.1	-1.91	12.33	4690
			5		0.2	0.20	0.40	2.0		2.0	1.0	2.0	0.20	6.08	6.67	1.13	49	6.3		71.29	93.1	-1.95	12.42	4780
Mg(OH) <sub>2</sub> pH Effects			5		0.2	0.25	0.45	2.0		2.0	1.0	2.0	0.25	6.05	6.63	1.14	48	6.3		71.22	93.1	-1.90	12.45	4850
	No Peroxide - Increasing Mg(OH) <sub>2</sub>	5/4	5		0.2	0.05	0.25			0.0	0.50		0.1	4.92	6.90				58.21	85.7	0.34	13.13		
			5		0.2	0.10	0.30			0.0	1.00		0.1	5.26	7.77				55.98	84.8	-0.30	13.88		
			5		0.2	0.15	0.35			0.0	1.50		0.1	5.61	8.04				54.51	84.3	-0.24	14.36		
			5		0.2	0.20	0.40			0.0	2.00		0.1	5.83	8.15				53.23	83.6	-0.21	14.65		
Mg(OH) <sub>2</sub> pH Effects			5		0.2	0.25	0.45			0.0	2.50		0.1	6.05	8.23				52.55	83.3	-0.24	14.85		
			5		0.2	0.00	0.00			0.0			#DIV/0!											

All experiments at 10% consistency

\*0.2% hydrosulfite in all Q stages

<sup>(a)</sup> or <sup>(b)</sup> data is repeated elsewhere in table

<sup>(a)</sup> or <sup>(b)</sup> data is repeated from elsewhere in table

\* residual not used, and values not used in average (done as repeat at later date)



# APPENDIX B – PREVIOUS IRVING PULP SAMPLE RESULTS

**Table 7. Irving Pulp sample – Phase 1 sample.**

Phase 1 data, 0.415 micron  $Mg(OH)_2$  particle size, except where noted

		time, hours	DTPA %	$Na_2SiO_3$ %	NaOH %	$H_2O_2$ %	$Mg(OH)_2$ %	Initial pH	Final pH	Residual $H_2O_2$ (g/l)	% $H_2O_2$ consumed	% $H_2O_2$ / point br gain	Brightness % ISO	L	a	b
Case 3 particle size	Brownstock	5	0.3	3%	1.44	2	0	10.72	7.32	0.65	71	7.51	60.92	86.98	0.53	12.52
	Control, 5 hr 0.415 micron	2	0.2%, 0.1%	0	0	2%	0.50	6.00	6.42	1.67	24	3.11	70.33	92.36	-1.59	12.13
	3.101 micron	2	0.2%, 0.1%	0	0	2%	0.50	5.28	6.50	1.66	25	3.15	68.63	91.28	-1.07	12.01
Case 4 varying Chelant in chelation and Peroxide stage	Q 0%, P 0%	5	No Q, 0.0%	0	0	2%	0.50	6.05	6.66	0.22	90	26	64.39	89.07	-0.48	12.52
	Q 0%, P 0.1%	5	No Q, 0.1%	0	0	2%	0.50	5.50	6.15	0.65	71	11.07	67.30	90.79	-0.90	12.44
	Q 0.10%, P 0.05%	5	0.10%, 0.05%	0	0	2%	0.50	5.65	6.22	1.10	50	6.15	69.04	91.64	1.14	12.20
	Q 0.15%, P	5	0.15%, 0.05%	0	0	2%	0.72%	6.50	6.36	0.86	61	7.19	69.41	92.24	-1.53	12.65
	Q 0.15%, P	5	0.15%, 0.05%	0	0	2%	0.50	6.12	6.05	1.41	36	4.19	69.51	91.95	-1.19	12.25
	Q 0.2%, P 0%	5	0.2%, 0.0%	0	0	2%	0.50	6.30	6.08	1.30	41	4.86	69.35	91.89	-1.29	12.26
	standard	5	0.2%, 0.1%	0	0	2% <sup>(a)</sup>	0.50	6.06	6.14	1.47	33	3.95	69.33	92.07	-1.42	12.51
residual liquor (R) replaces some peroxide (a), (b), source of residual peroxide	R 0.8%, MH 0.5%	5	0.2%, 0.1%	0	0	2% <sup>(a)</sup>	0.50	5.80	6.10	1.45	34	4.18	69.10	91.71	-1.19	12.30
	R 0.8%, MH 0.25%	5	0.2%, 0.1%	0	0	2% <sup>(b)</sup>	0.25	5.50	5.60	1.70	23	3.45	67.50	90.80	-0.80	12.27
	fresh P, MH 0.5%	5	0.2%, 0.1%	0	0	1.27	0.50	5.90	6.10	0.80	64	9.51	67.60	91.20	-1.14	12.74
	fresh P, MH 0.25%	5	0.2%, 0.1%	0	0	1.24	0.25	6.00	5.90	0.97	56	11.26	65.90	90.10	-0.70	12.55
Chelation with Hydrosulfite (HS)	Mill chelated	5	0.3%, 0%	3	1.44	2%	0	10.80	7.30	0.42	81	10.30	68.80	91.58	-1.16	12.27
	HS 0.2%	5	0.3%, 0%	3	1.44	2%	0	10.70	7.40	0.65	71	7.69	70.10	92.13	-1.28	12.02
	HS 0.2% / $N_2$	5	0.3%, 0%	3	1.44	2%	0	10.90	7.40	0.62	72	8.18	69.70	92.01	-1.33	12.20
	HS 0.2% / $N_2$	5	0.15%, 0.05%	3	0	2	0.50	6.10	6.00	1.35	39	4.89	68.80	91.71	-1.09	12.46
	HS 0.2% / $N_2$	5	0.2%, 0.1%	3	0	2% <sup>(a)</sup>	0.50	5.90	6.10	1.59	28	3.30	69.30	91.79	-1.08	12.24